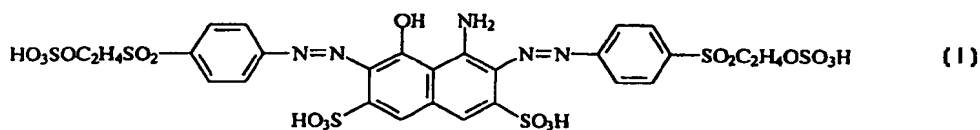




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09B 67/22, 67/24	A1	(11) International Publication Number: WO 00/43455 (43) International Publication Date: 27 July 2000 (27.07.00)
(21) International Application Number: PCT/US00/00486 (22) International Filing Date: 19 January 2000 (19.01.00) (30) Priority Data: 09/233,455 20 January 1999 (20.01.99) US 09/346,731 2 July 1999 (02.07.99) US (71) Applicant: EVERLIGHT USA, INC. [US/US]; 10570 Southern Loop Boulevard, Pineville, NC 26134 (US). (72) Inventors: LAI, Bao-Kun; No. 12, Alley 8, Lane 268, Sin-shin Road, Tien-Shin Village, Ta-Yuan County, Tau-Yuan Hsien, Taiwan (TW). SONG, Der-Chin; Floor 5, No. 57-2, Jin-Fon 5 Street, Chung-Li, Tau-Yuan Hsien, Taiwan (TW). (74) Agents: FICHTER, Richard, E. et al.; Bacon & Thomas, PLLC, 4th Floor, 625 Slaters Lane, Alexandria, VA 22314 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: REACTIVE DYE COMPOSITION



(57) Abstract

A reactive dye composition comprising (a) at least a black or navy reactive dye with good color fastness to laundering-oxidative bleach; and (b) at least a red, orange, yellow or other shade of reactive azo dye. The reactive dye composition of the present invention may further comprise (c) a black reactive dye of formula (I). The dye composition of the present invention is suitable for use in dyeing fiber material. It has good properties in build-up, wash fastness, ease of wash-off, and levelness, especially excellently performing in the property of good color fastness to laundering-oxidative bleach.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

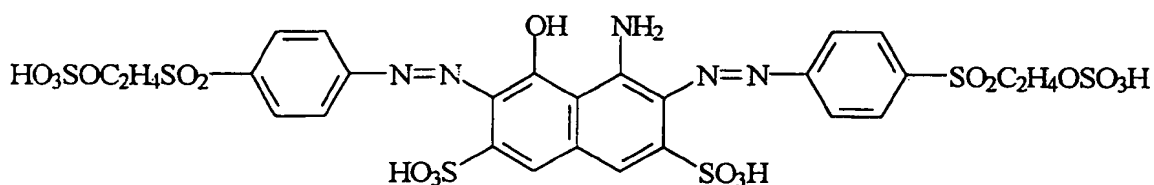
REACTIVE DYE COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a reactive dye composition, in particular relates to a black or navy reactive dye composition suitable for use in dyeing fiber materials. It has good property in color fastness to laundering-oxidative bleach.

10 BACKGROUND OF THE INVENTION

So far, it is difficult to find a single reactive dye which can produce a good build up property in black shade. In order to get a good build up property in black shade, a reactive dye composition which contains a number of reactive dye components has been used. One black or navy reactive dye (for example, the following formula (I) black reactive dye) as the major component



(I)

is usually mixed with red, orange, yellow or other shade reactive dye components to get the black reactive dye composition.

Black reactive dye compositions are already known from Japanese Patent Laid-open No. 58-160362, 63-178170, 1-315469, 2-73870, 2-202956, 8-104822, 8-253697, US Pat. No. 5,445,654 and US Pat. No. 5,611,821.

Due to strict requirements in energy saving and environmental regulations, advanced washing machines and highly efficient detergents have been continuously developed. The use of highly efficient detergents containing blaching agents greatly improves the cleanness of washed material. However, washed material fades soon after several washings. This problem becomes worse if washed material was dyed by the reactive black dye composition based on the major component of formula (I). Therefore, there is a strong demand for a reactive black or navy dye composition having good property in color fastness to laundering-oxidative bleach.

A reactive black or navy dye composition which comprises the above formula (I) black reactive dye as the major component and mixed with a number of reactive azo dyes fades soon after several washings. The reason is the poor property of the reactive black dye composition in color fastness to laundering-oxidative bleach. Therefore, washed material is caused to fade by the bleaching agent present during laundry.

If each dye component of the dye composition has different color fastness to laundering-oxidative bleach, the washed material may be caused to fade and to change its hue as well. The current commercial black dyes commonly have this drawback. Because the formula (I) mainly used in current commercial black dyes has worse property than the other shade components in color fastness to laundering-oxidative bleach, the washed black or navy material is caused hue change into brownish.

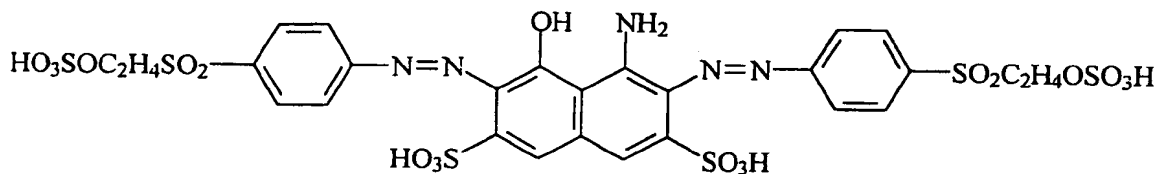
In order to eliminate the aforesaid problem, there is a suggestion to select red, orange, yellow, or other shades of reactive dye components having similar color fastness to laundering-oxidative bleach to the formula (I). A black dye

composition prepared according to this suggestion may eliminate the hue change, however it cannot prevent the washed material from being caused to fade by the bleaching agent.

5 SUMMARY OF THE INVENTION

It is one object of the present invention to provide a reactive dye composition that is suitable for use in exhaustion, printing, or continuous dyeing to provide good dyeing properties. Other objects of the present invention are to provide a reactive
10 dye composition which has good properties in build-up, wash fastness, wash-off, levelness and color fastness to laundering-oxidative bleach.

The black or navy dye composition of the present invention comprises: (a) at least a black or navy reactive dye with good
15 color fastness to laundering-oxidative bleach; and (b) at least a red, orange, yellow or other shade of reactive azo dye. The reactive dye composition of the present invention may further comprise (c) a black reactive dye of the following formula (I).



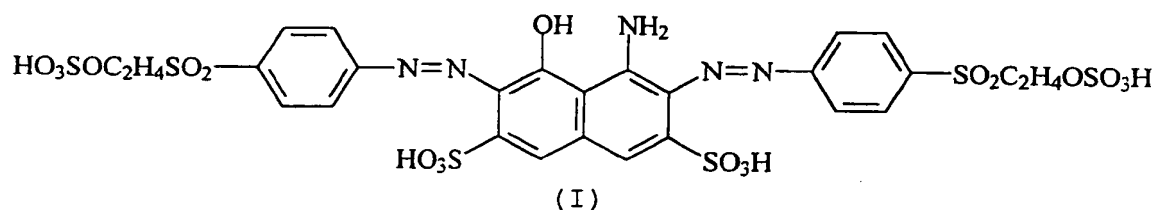
(I)

In order to improve the characteristics of the reactive
25 dye composition, a black or navy reactive dye with good properties in wash fastness and color fastness to laundering-oxidative bleach is added. This composition effectively eliminates material from hue change, or fading due

to the effect of a bleaching agent.

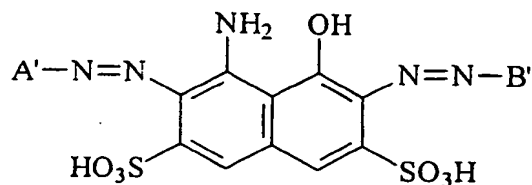
DESCRIPTION OF THE PREFERRED EMBODIMENTS

A black or navy dye composition in accordance with the present invention generally comprises (a) at least a black or navy reactive dye with a good color fastness to laundering-oxidative bleach and wash fastness, (b) at least a red, orange, yellow or other shade of reactive azo dye. If it is necessary, the reactive dye composition of the present invention can further comprise component (c) a black reactive dye of the following formula (I).



There is no special limitation on the black or navy reactive dye of component (a). Any black or navy reactive dye has good properties in wash fastness and color fastness to laundering-oxidative bleach that is compatible to the black reactive dye of formula (I) in dyeing properties, fixation, and dying affinity can be used.

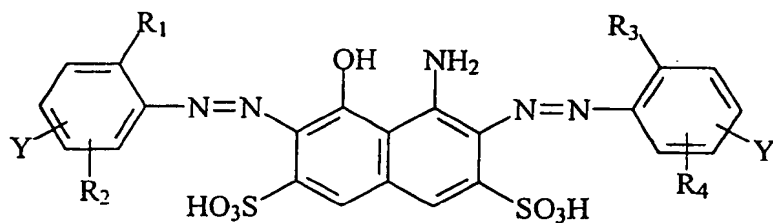
Preferably, the black or navy reactive dye of component (a) is a compound having the following formula (II)



(II)

wherein A' and B' are each independent of the unsubstituted or substituted aromatic group, for example by halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, sulfonyl or amino groups. The compound of formula (II) and the black reactive dye of formula (I) have a similar structure. Both of them are reactive dyes, containing 1-amino-8-hydroxynaphthyl-3,6-disulfonic acid derivative structure, and the compound of formula (II) have some substituted.

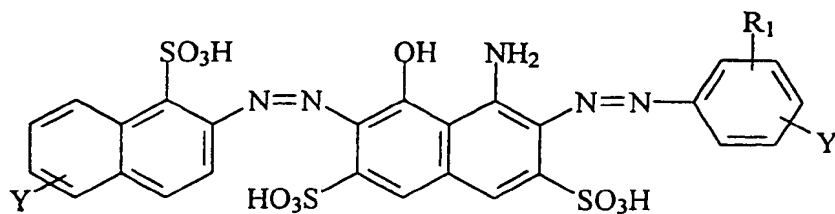
Examples of formula (II) are:



(III)

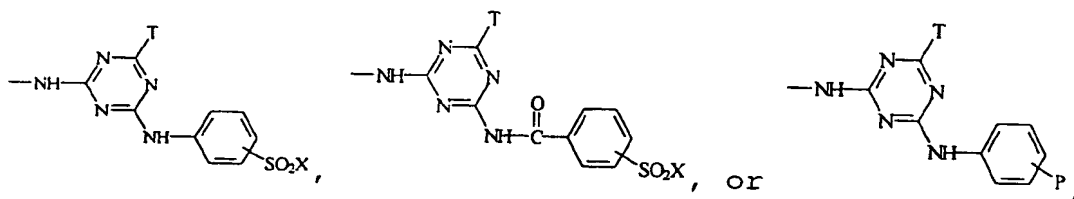
15

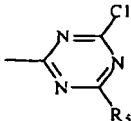
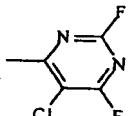
or



(IV)

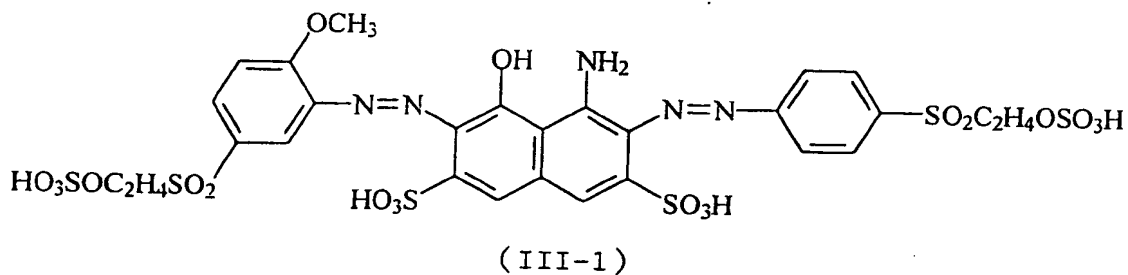
wherein Y and Y', each independent, is $-\text{SO}_2\text{X}$, $-\text{NH}-\text{W}$,

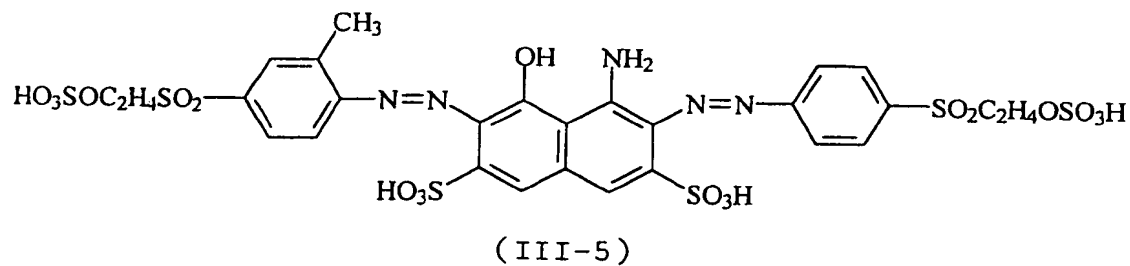
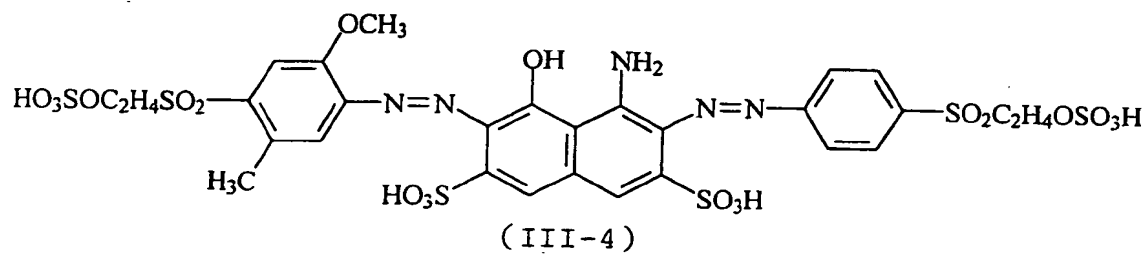
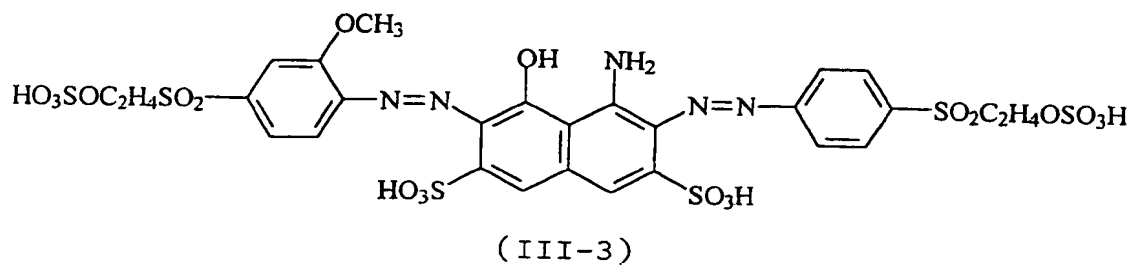
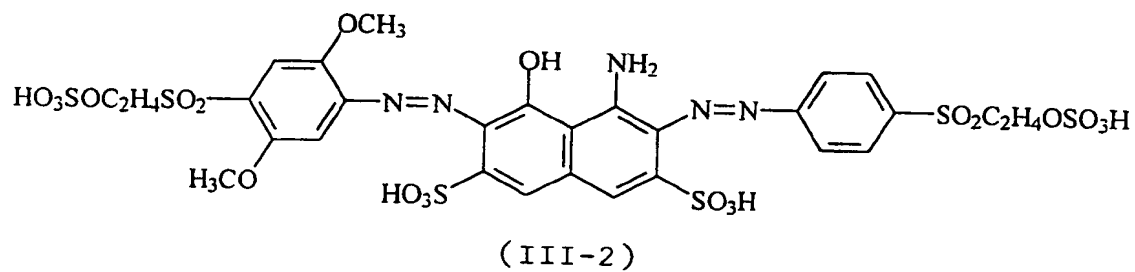


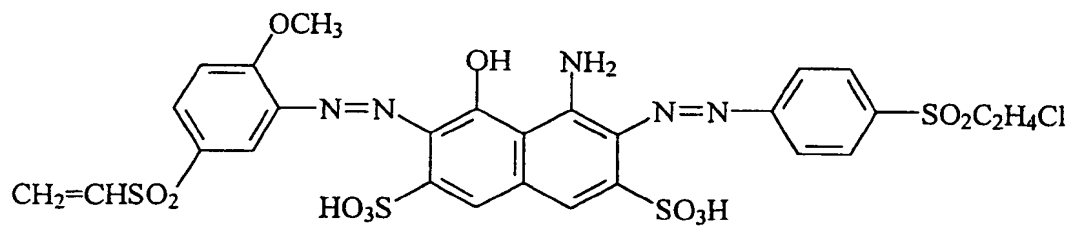
wherein W is , or , X is $-\text{OH}$, $-\text{CH}=\text{CH}_2$,

- 5 $-\text{C}_2\text{H}_4\text{OSO}_3\text{H}$, or $-\text{C}_2\text{H}_4\text{Cl}$, T is $-\text{NHCN}$, $-\text{F}$, or $-\text{Cl}$, P is hydrogen, halogen, C_1 - C_4 alkyl, or C_1 - C_4 alkoxy, R_5 is $-\text{Cl}$ or C_1 - C_4 alkoxy,
- R_1 , R_2 , R_3 and R_4 , each independent, is hydrogen, halogen, hydroxyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or sulfonyl groups and
- 10 at least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen.

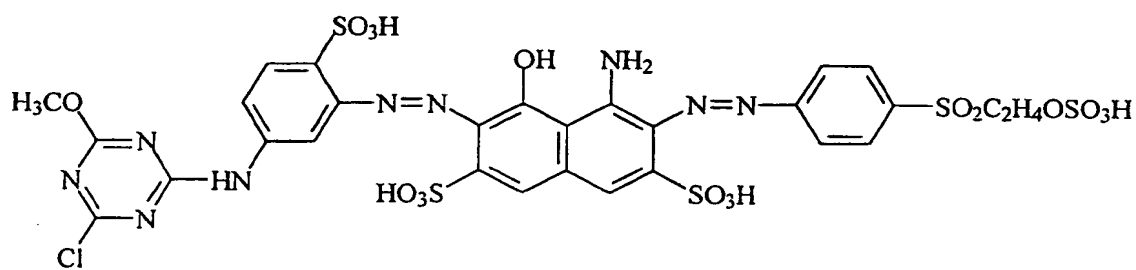
More preferable examples of formula (III) and formula (IV) are:





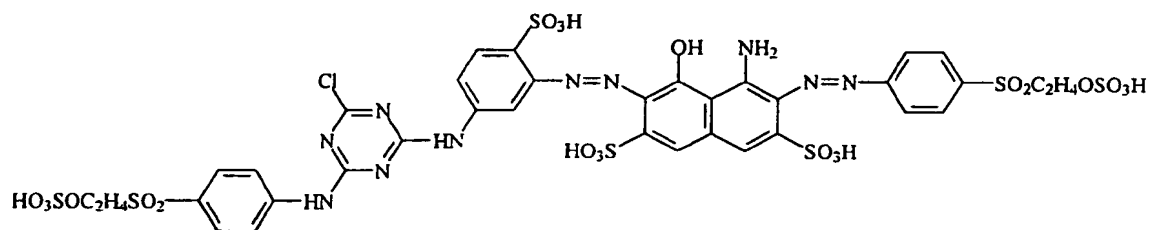


(III-6)

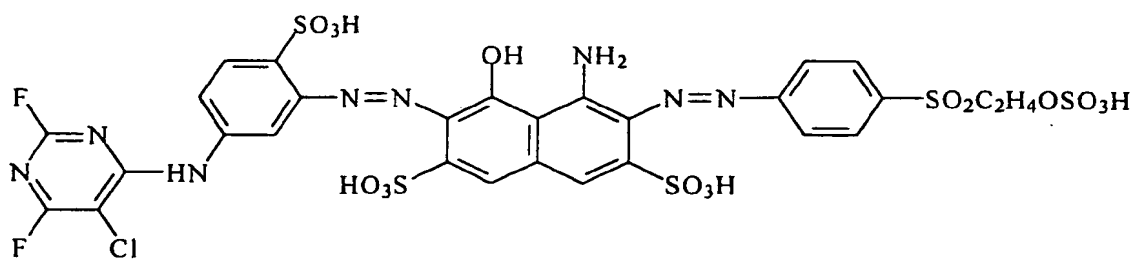


5

(III-7)

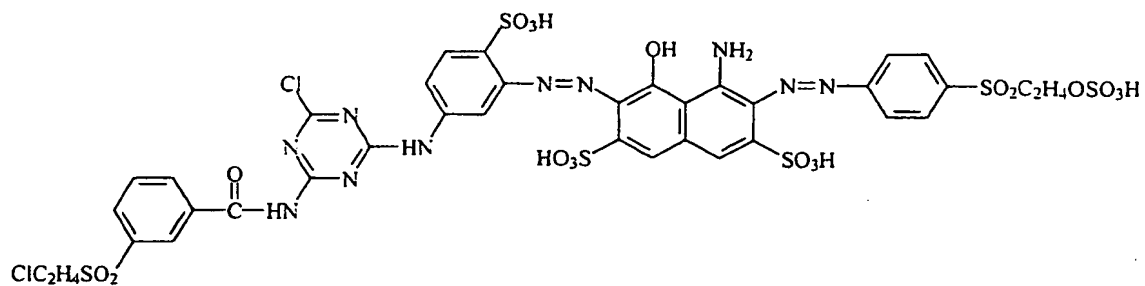


(III-8)

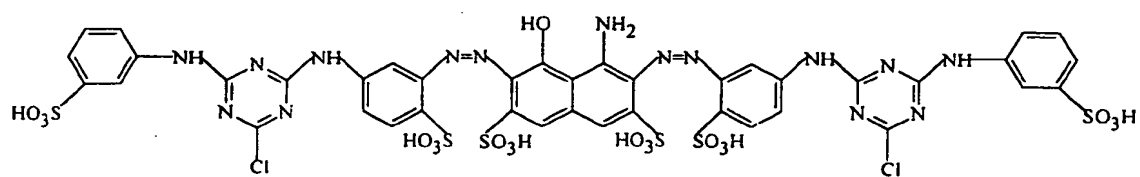


10

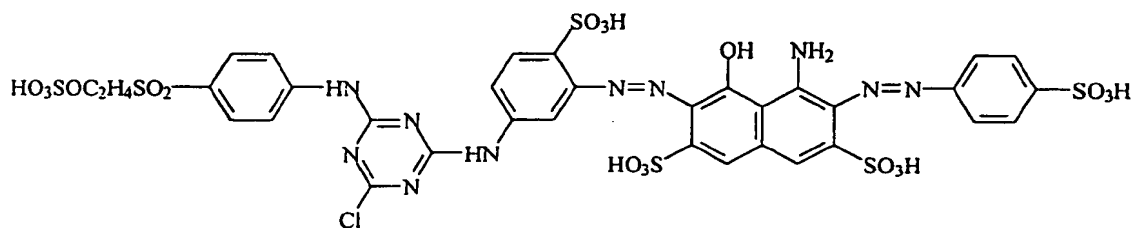
(III-9)



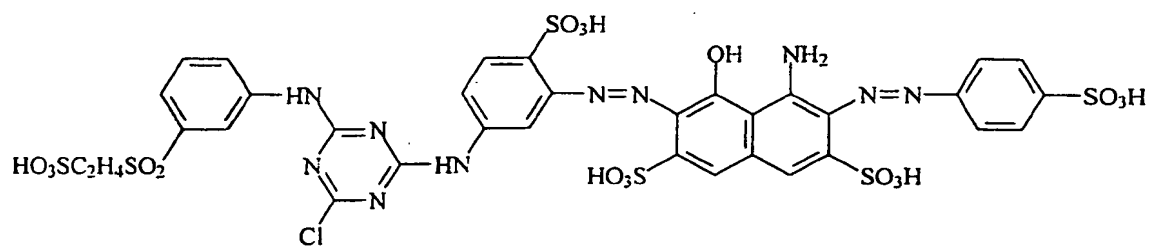
(III-10)



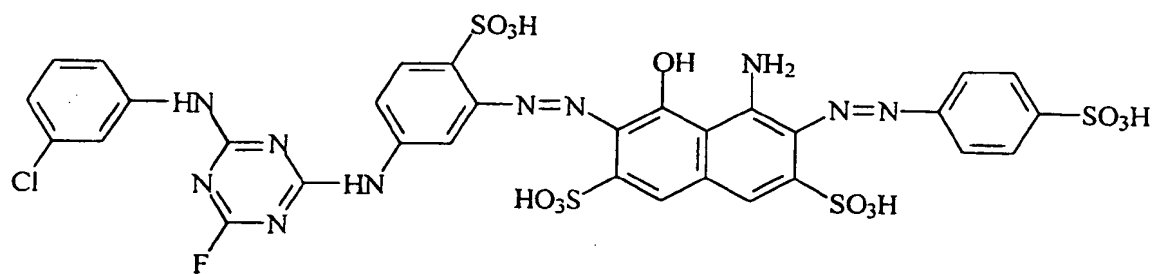
(III-11)



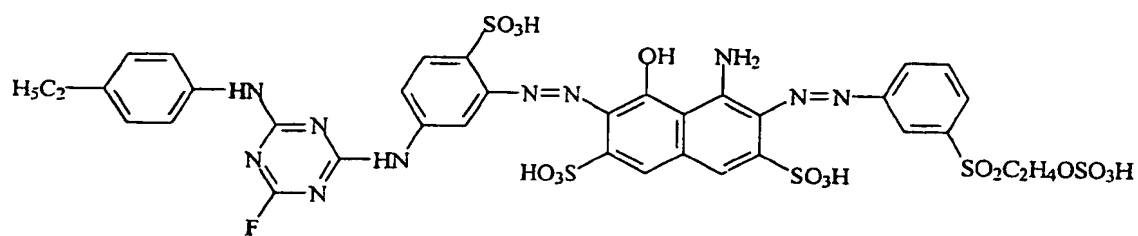
(III-12)



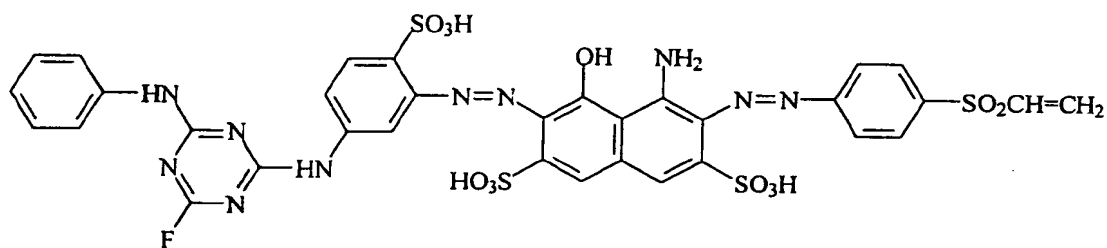
(III-13)



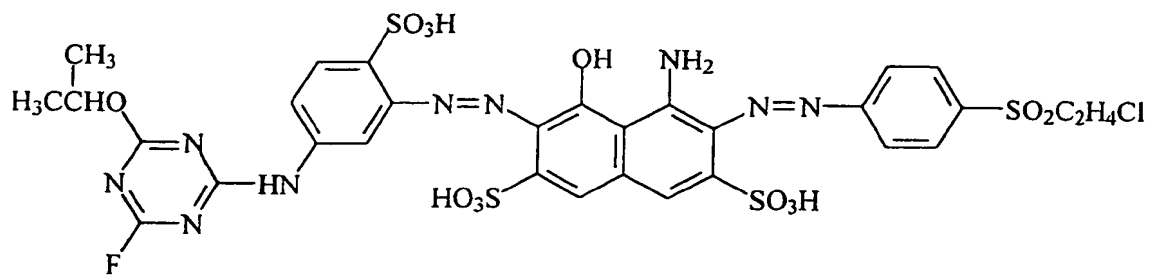
(III-14)



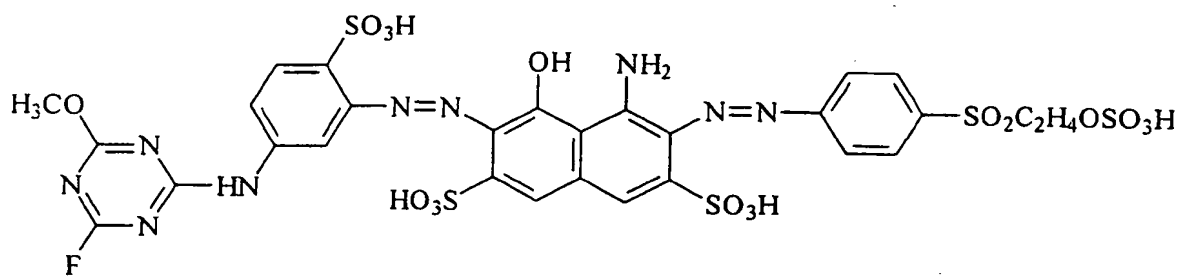
(III-15)



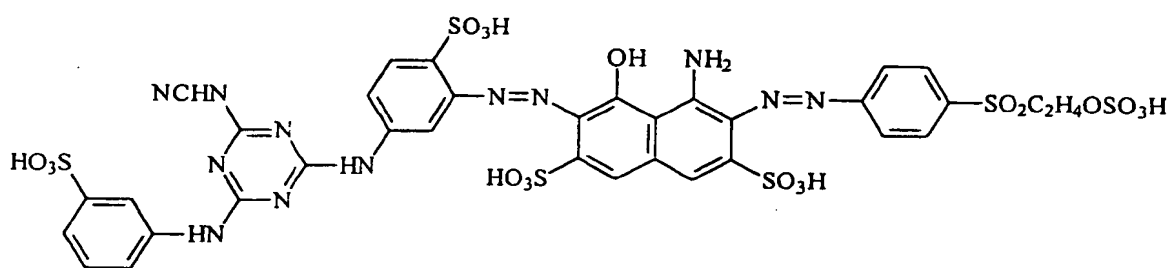
(III-16)



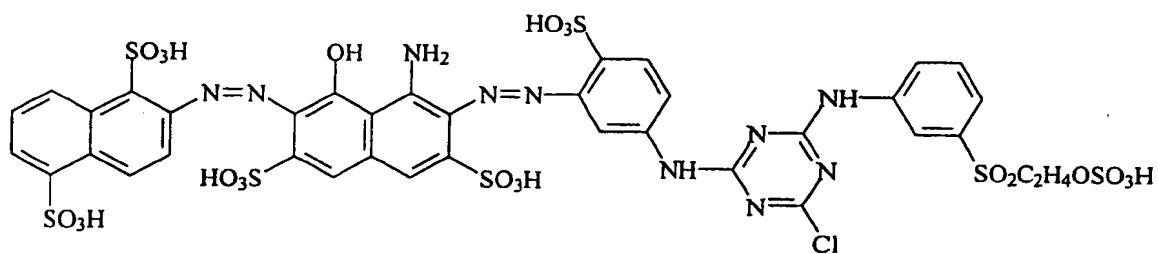
(III-17)



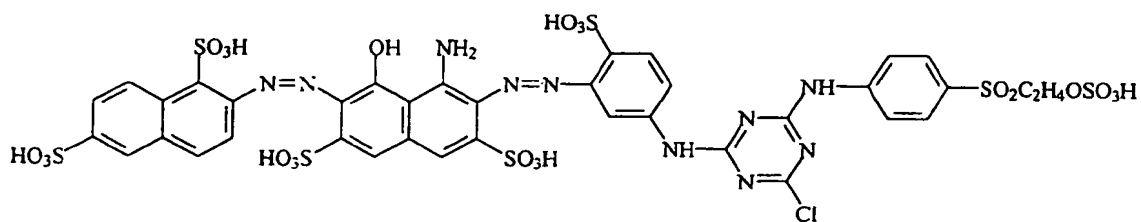
(III-18)



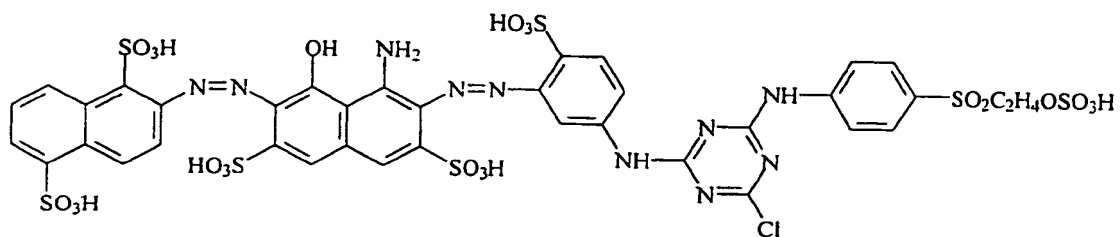
(III-19)



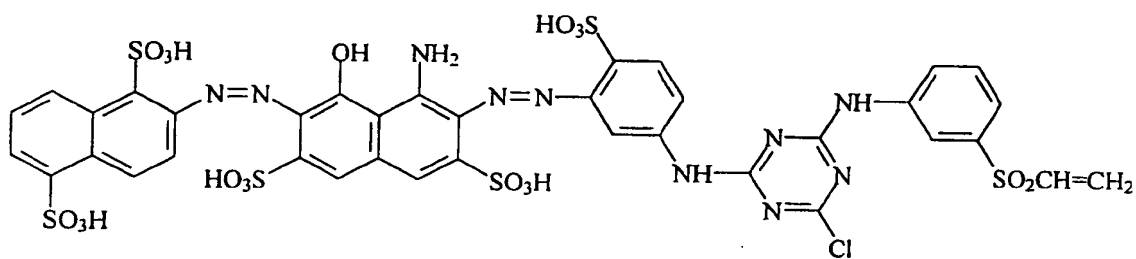
(IV-1)



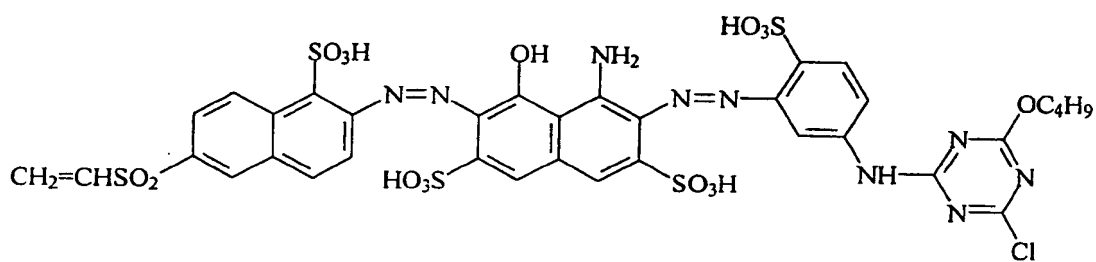
(IV-2)



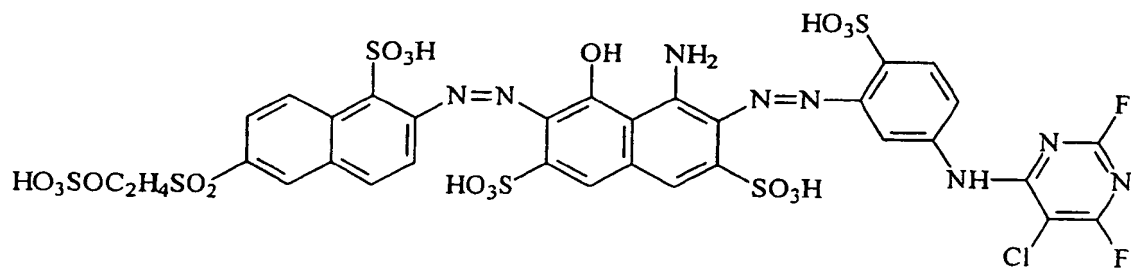
(IV-3)



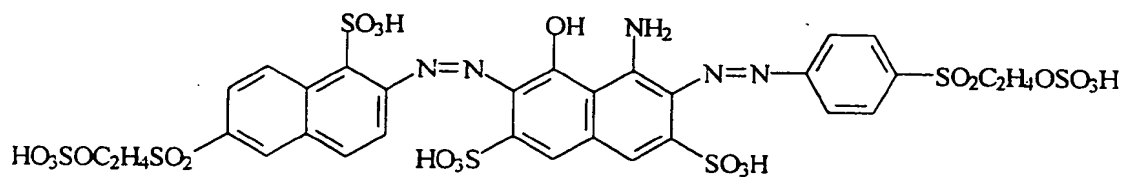
(IV-4)



(IV-5)



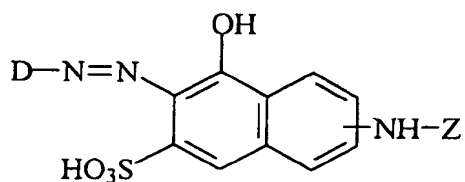
(IV-6)



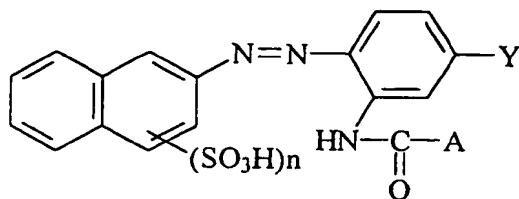
(IV-7)

There is no special limitation on the red, orange, yellow or other shade of reactive azo dye of component (b). Any red, orange, yellow or other shade of reactive azo dye, containing good build-up property, is compatible to component (c) the black reactive dye of the formula (I) in dyeing properties, fixation and dying affinity, can be used.

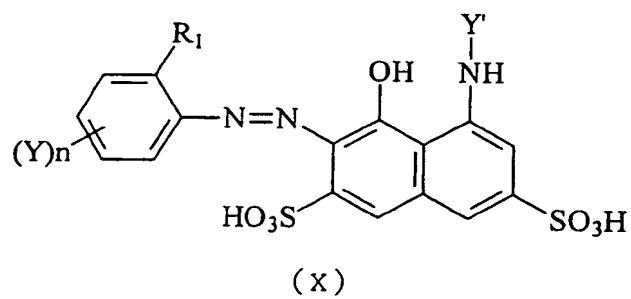
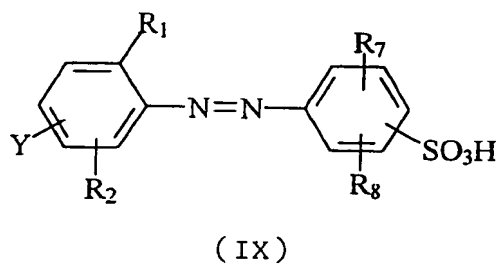
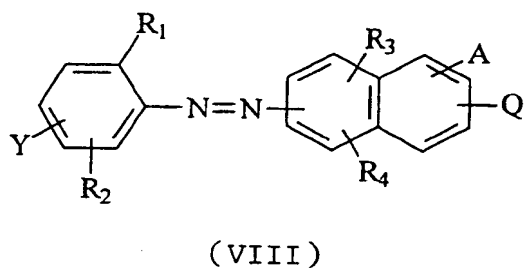
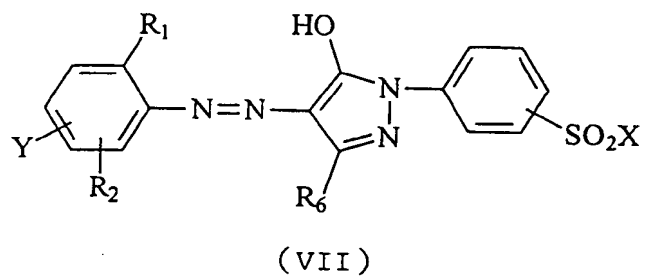
Preferably, the examples of red, orange, yellow or other shade of reactive azo dye of component (b) are:

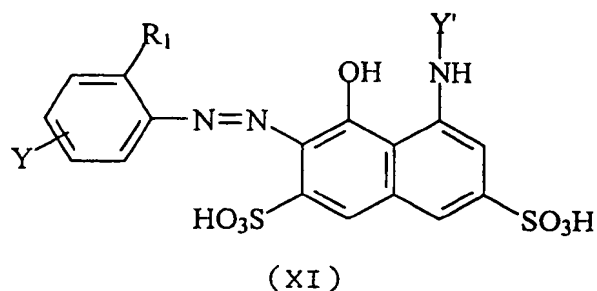


(v)

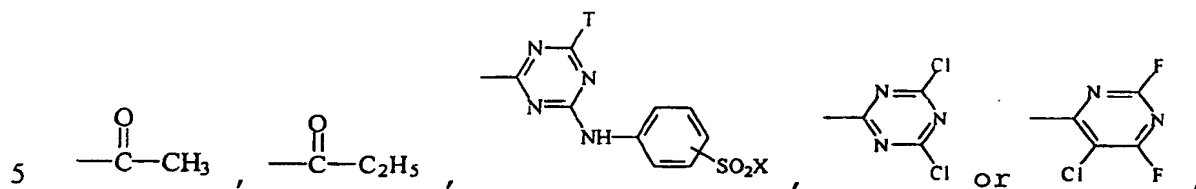


(VI)

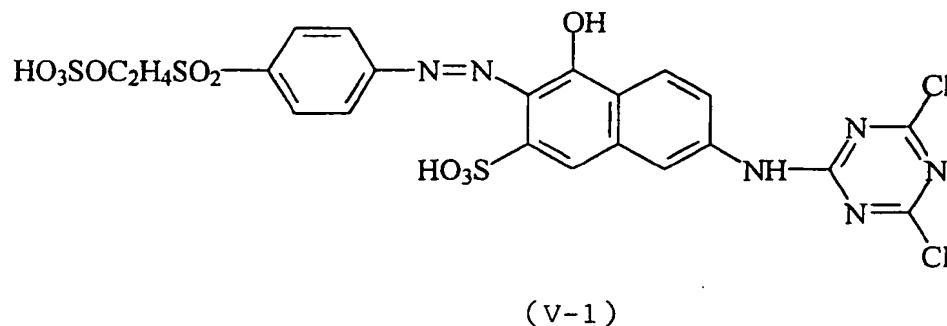


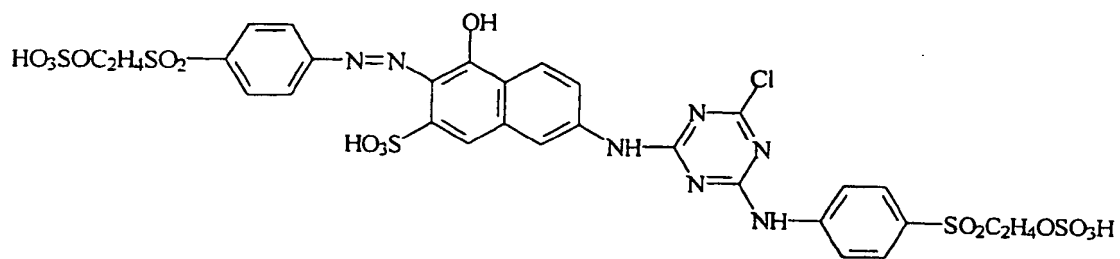


wherein D is , or , Z is

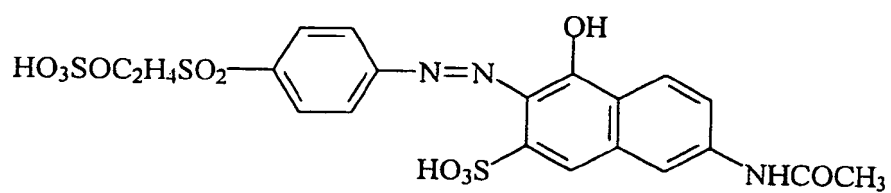


A is —OH, —NH₂ or —CH₃, R₆ is —CO₂H, —NH₂ or —CH₃,
 Q is —CO₂H or —SO₃H, R₇ and R₈, each independent, is hydrogen,
 C₁-C₄ alkyl, amino or amino derivatives, n is 0, 1, 2, or 3,
 10 wherein X, Y, Y', R₁, R₂, R₃, R₄ and T are defined as the above.
 More specific examples of component (b) are:

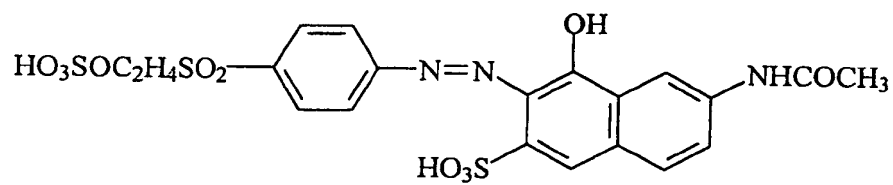




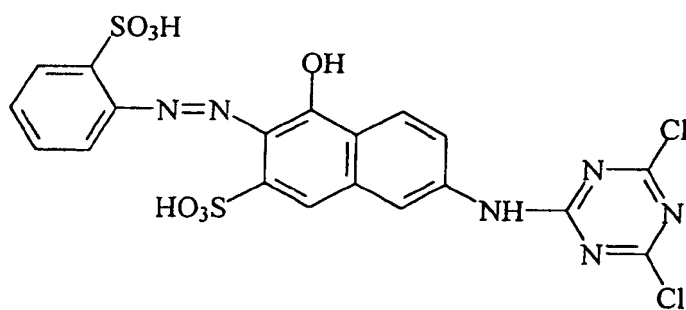
(V-2)



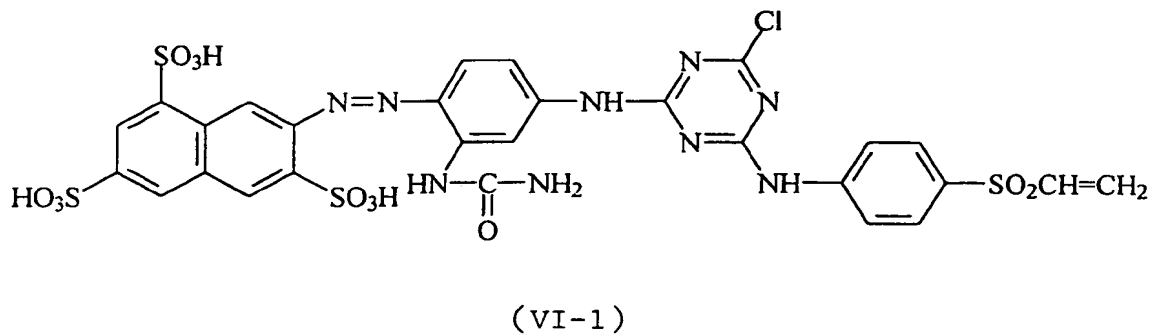
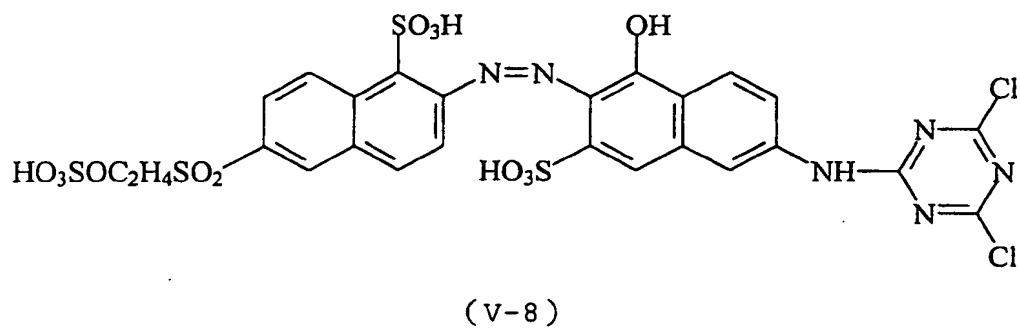
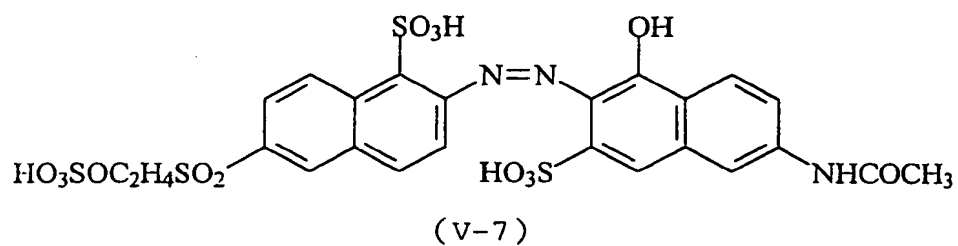
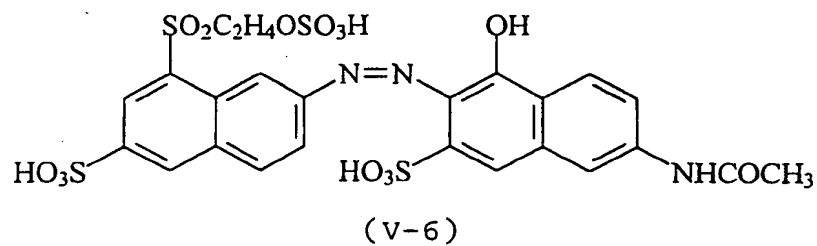
(V-3)

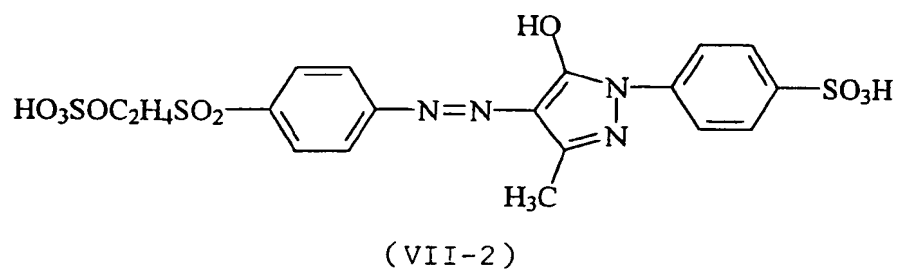
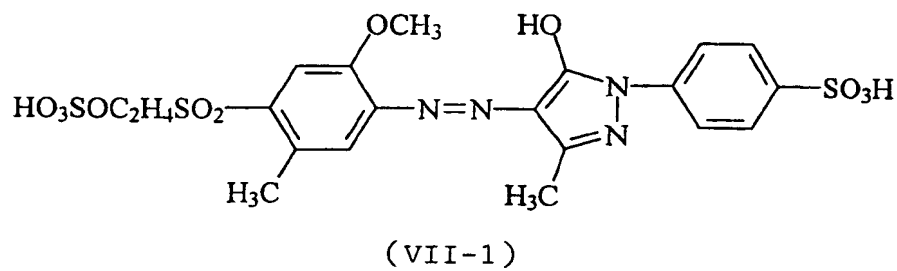
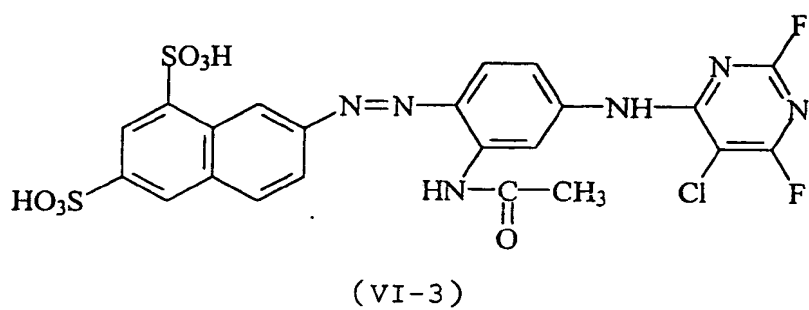
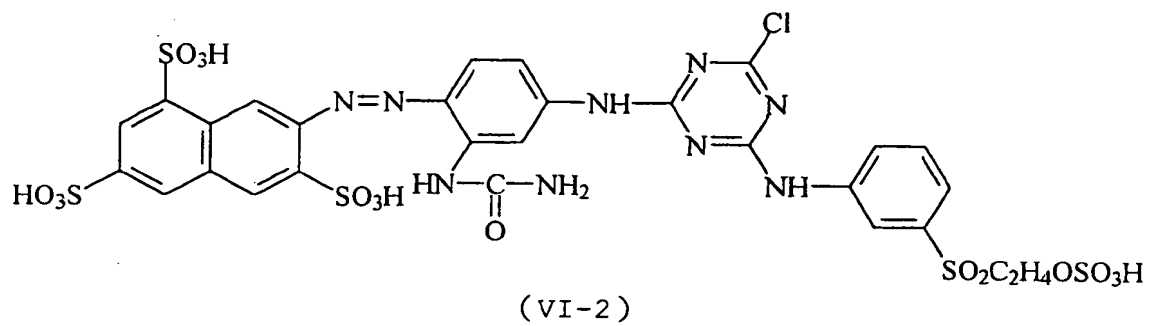


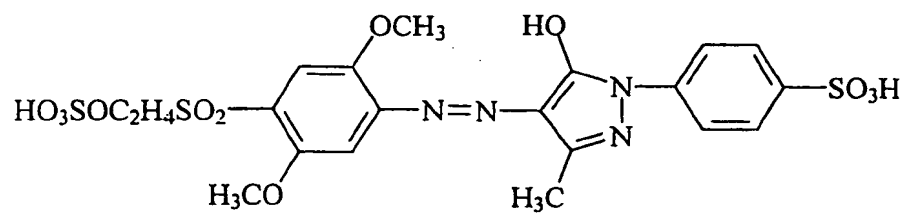
(V-4)



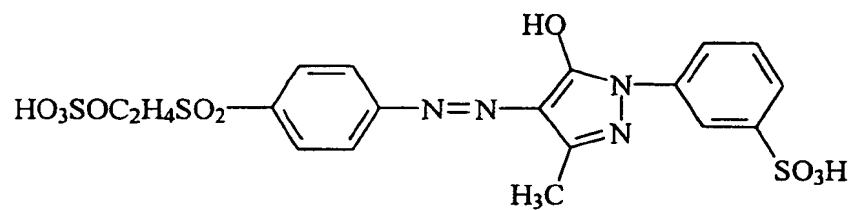
(V-5)



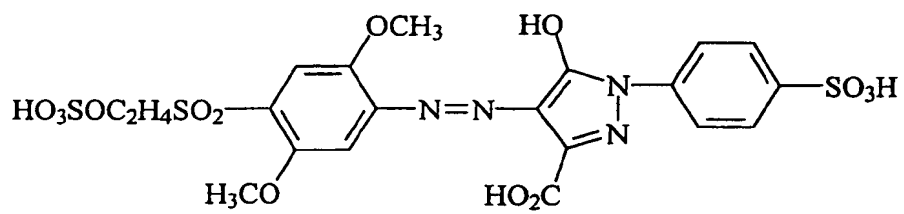




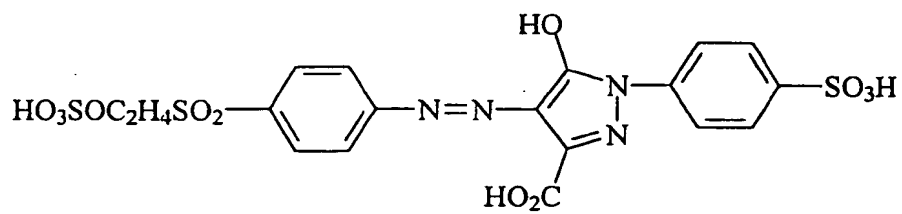
(VII-3)



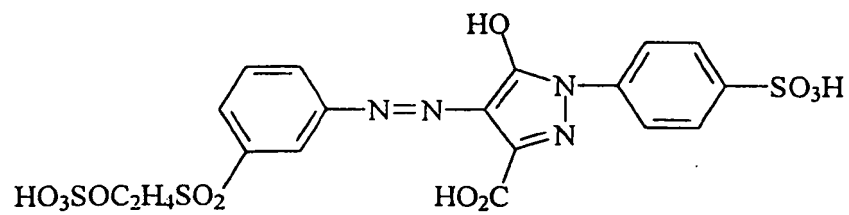
(VII-4)



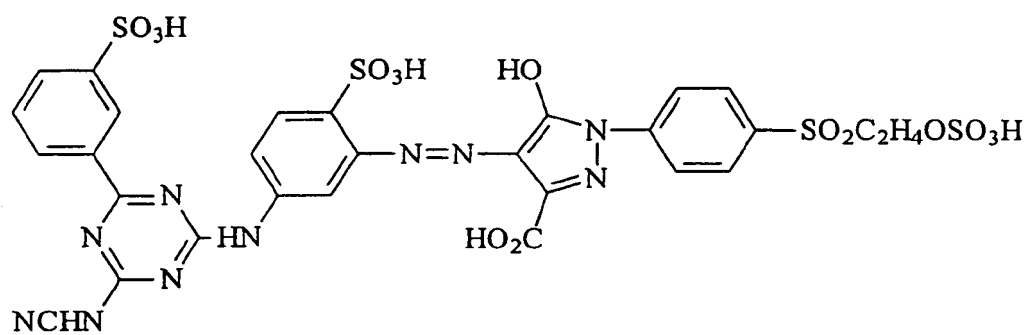
(VII-5)



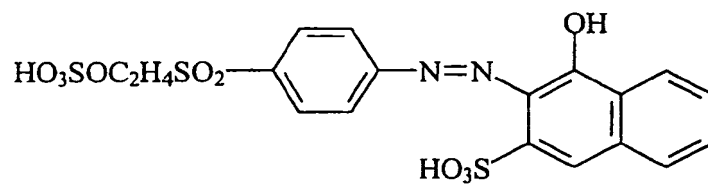
(VII-6)



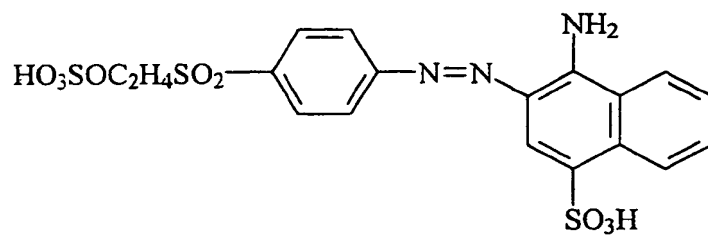
(VII-7)



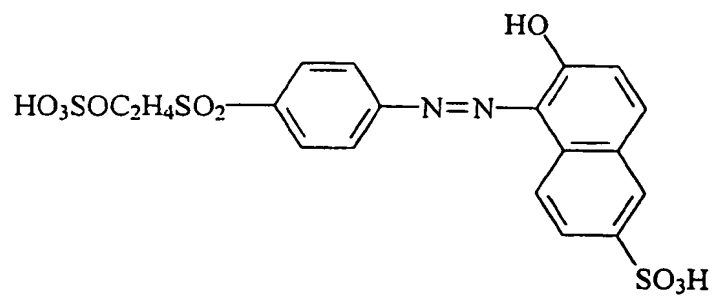
(VII-8)



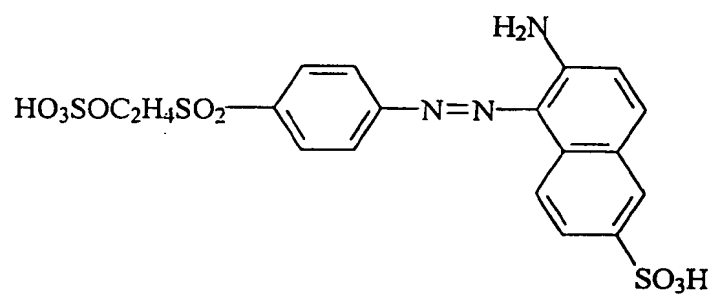
(VIII-1)



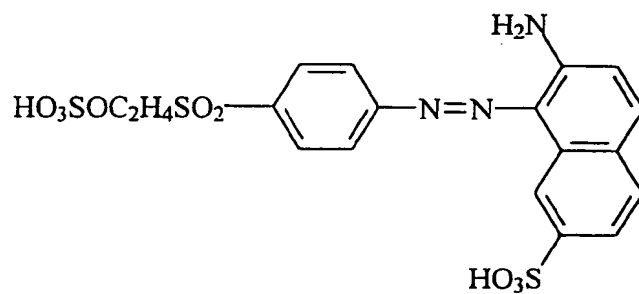
(VIII-2)



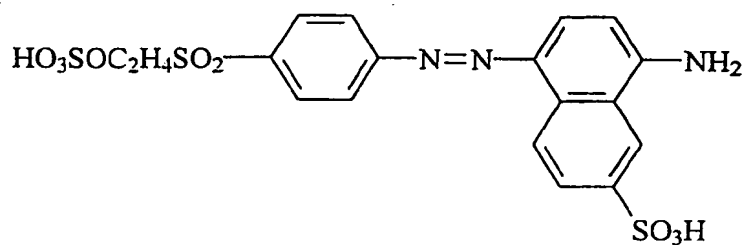
(VIII-3)



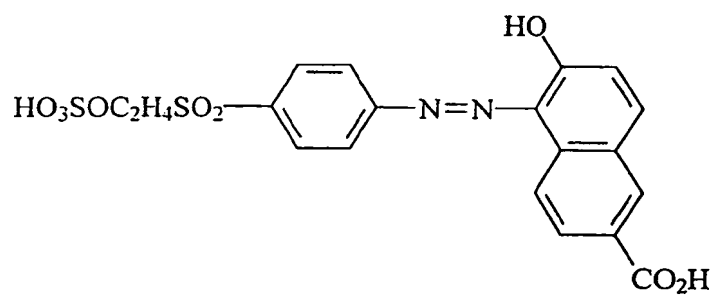
(VIII-4)



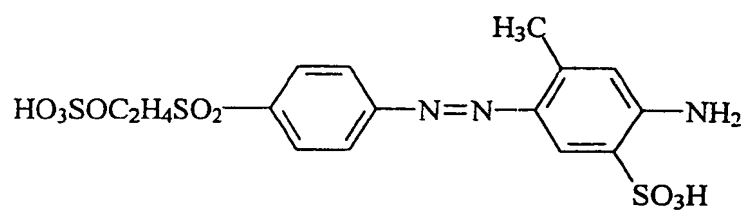
(VIII-5)



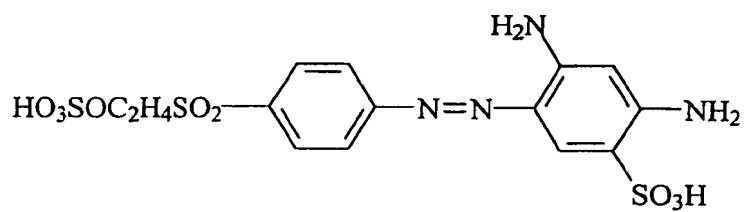
(VIII-6)



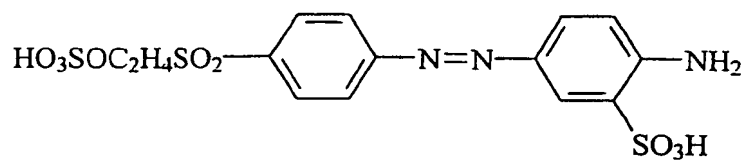
(VIII-7)



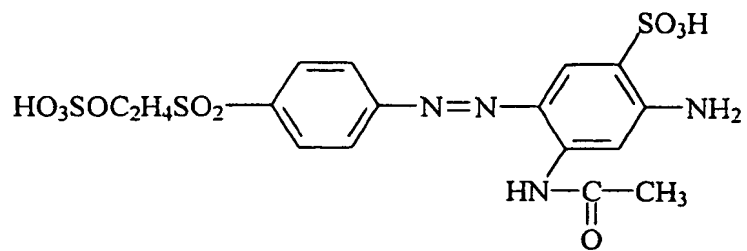
(IX-1)



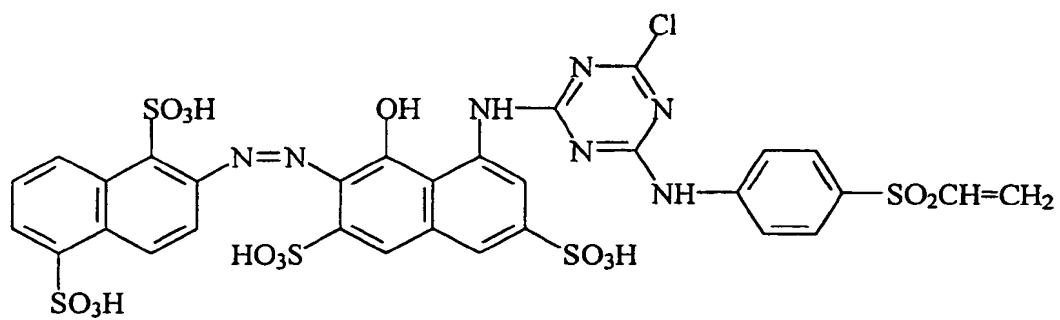
(IX-2)



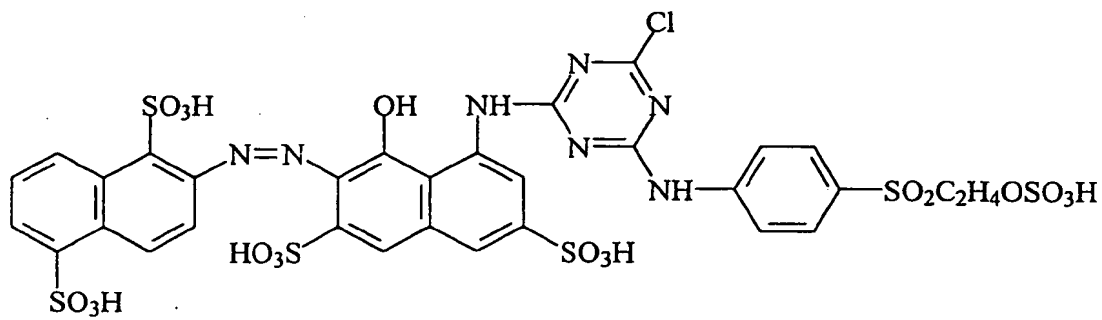
(IX-3)



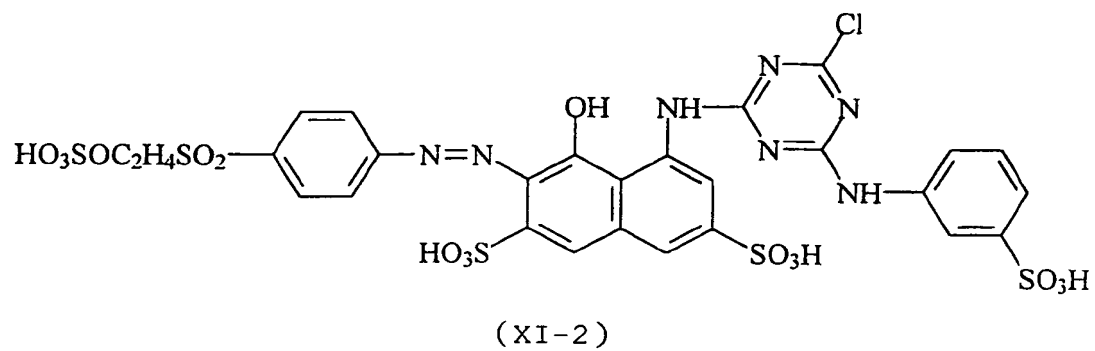
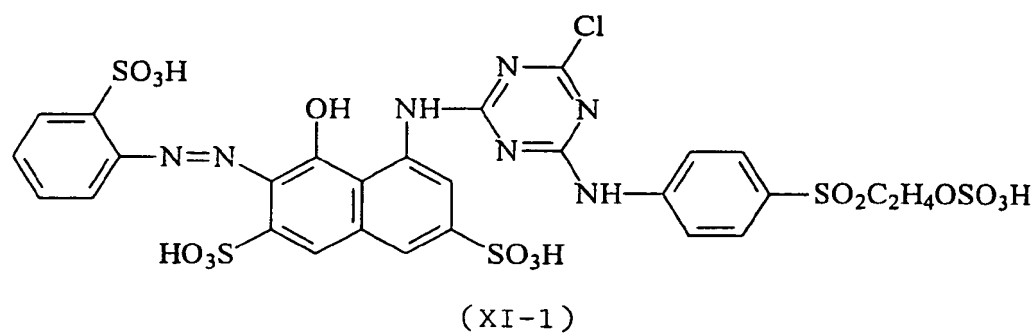
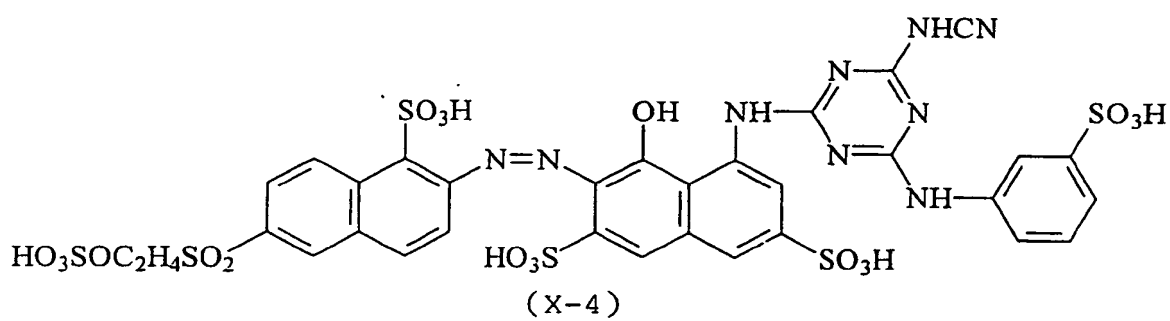
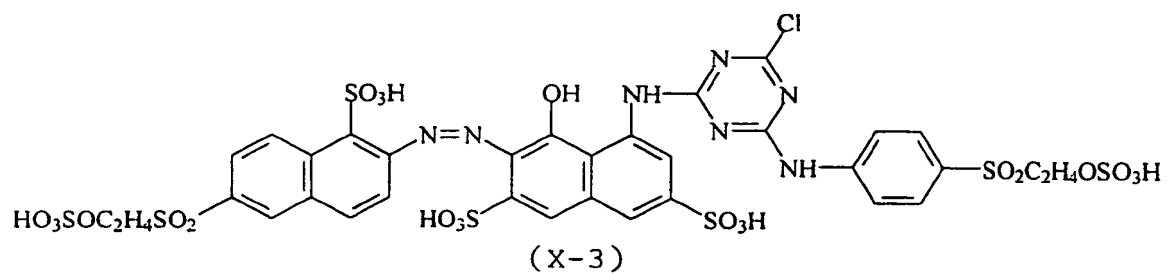
(IX-4)

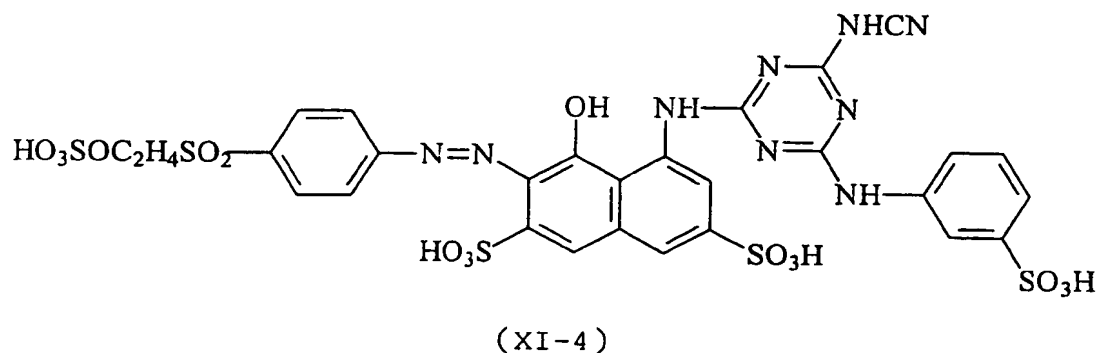
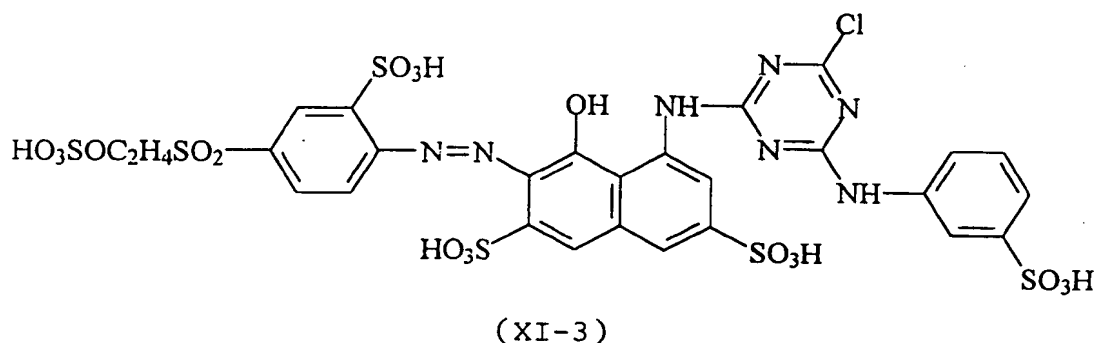


(X-1)



(X-2)





The compositions of the present invention can be prepared in several ways, i.e. by using the separately prepared dye component to mix together to make power, granular and liquid forms, or by mixing a number of individual dyes as a dyeing recipe in a dye house.

The dyestuff of the present invention can be in the form of powder, granular or liquid; and an auxiliary reagent, for example, a retarding agent, leveling agent, assistant agent, surfactant, or dispersing agent may be added.

The dyestuffs of the present invention all contain an anion group, such as a sulfonic acid group. For convenience in the statement, they are expressed as free acid in the

specification. When the dyestuff of the present invention is manufactured, purified or used, it often exists in the form of water soluble salt, especially an alkaline metallic salt, such as sodium salt, potassium salt.

5 The ratio of each dye component can be changed in a wide range. In general, the minimum relative weight percentage for each dye component is 3%, and the maximum relative weight percentage is 90%.

10 The black dye composition of the present invention can be widely applied to dyeing a greater range of textiles that contain a hydroxyl group or amide group, etc., such as wool, silk, polyamide, and natural or synthetic fiber; and also cellulose fiber like cotton, linen, artificial cotton, and artificial linen, etc. The dyeing method used is the one
15 generally used when a reactive dyestuff is applied. An known reactive dyeing application of cellulose is described a follow : the dyes are applied in an aqueous bath and required inorganic electrolyte (common salt or sodium sulphate) to achieve high level of exhaustion. The covalent bond connecting a dye and
20 cellulose fiber is formed on the addition of alkali (soda ash, sodium bicarbonate or caustic soda).

25 For cellulose fiber, the black dye composition of the present invention is a dye composition with great industrial value. Dyed material with various good dyeing properties can be obtained, especially the properties of build-up, color
fastness to laundering-oxidative bleach, wash fastness, ease of wash-off and levelness.

30 Whether dyes have good color fastness to laundering-oxidative bleach or not were determined by their color change value (ΔE) and gray scale rating for assessing color change.

The color change was obtained through following procedures. An unmercerized cotton knitting was dyed with 3% on the weight of fiber of dye. The dyed material was subsequently treated with the procedures described in British Standard BS 1006; UK-TO colour fastness to domestic laundering-oxidative bleach, 1998. The color of the dyed material was measured by Macbeth, Color-Eye 3100. The color change ΔE was obtained with colour formular CIE Lab and CMC(2:1). If the gray scale rating of a dye is above 3-4 or the ΔE of a dye is less than 3 and on-toning fading , the dye is evaluated as it with good color fastness to laundering-oxidative bleach .

More detailed examples were used to illustrate and explain the present invention. The examples below, simply given for demonstration, must not be taken to limit the scope of the invention.

In these examples, the compound is represented by free acid, but its actual form can be metallic salt, especially sodium salt. In these examples, parts is counted as weight, temperature is Celsius $^{\circ}\text{C}$.

Example 1

Take formula (III-1) dye 86 parts and formula (VIII-2) dye 14 parts mixed together to get a homogeneous mixture. Then use the following procedure to carry out dyeing and color fastness to laundering-oxidative bleach test.

Dye Procedure:

a. Take the above dye composition two parts and completely dissolve in 100 parts distilled water to get dye solution.

- b. Then take the dyeing bottle washed with distilled water and put 12 parts dye solution into the bottle. Finally add 6.4 parts Glauber's salt into the bottle.
- c. Distilled water is added to the bottle to make up to total
5 80 parts.
- d. Place eight parts unmercerized cotton knitting into the dyeing bottle.
- e. The top of the bottle is covered with a lid and shaken.
- f. Put dyeing bottle into a thermobath at 60 °C and shake for
10 20 minutes. Then add 7.5 parts sodium carbonate (320g/l) to the bottle and keep at the same temperature for 90 minutes. The fabric is taken out and washed with cold water, then put into a big stainless bucket and washed with hot water for 10 minutes. Then put fabric into another big stainless
15 bucket with 2.0 g/l soaping agent, and wash with boiling water for another 10 minutes.
- g. The fabric is taken out, cold rinsed and dried.

Color fastness to laundering-oxidative bleach response test:
20 (References: BS 1006; UK-TO color fastness to domestic laundering-oxidative bleach response, 1998)

- a. Put the dried test cloth obtained from dyeing in an incubator under relative humidity 65% and temperature 20°C for 4 hours, then take 10x5cm² of the cloth for test.
- 25 b. Prepare a test solution by dissolving 10g ECE soap that contains no phosphorus, 12g sodium perborate, and 1.8g TAED (tetra acetyl ethylenediamine) in 1,000 ml distilled water.
- c. Take the test cloth and the test solution thus obtained, the bath ratio is 1:100 (cloth : solution), and put it in a 550
30 ml steel cylinder.

- d. Close the steel cylinder, then put the steel cylinder in a wash fastness test machine under, the temperature from 30°C raise to 60°C by 2°C /min, then under test temperature 60°C for 30 minutes.
- 5 e. Remove the cloth from the steel cylinder after the test, then wash the cloth with clean water, and then dry the cloth.
- f. Determination of test result: use Macbeth, Color-Eye 3100 to examine the color based on the color change (ΔE) of color formular CIE Lab and CMC (2:1) standards. The quality is acceptable when the gray scale for assessing change of color rating is higher than 3-4 degrees or $\Delta E < 3$, and on-tone fading appears. Those kinds of dye compositions can be described as "compositions having good property in color fastness to laundering-oxidative bleach response".

15

Example 2 to Example 24

Take composition examples in the following table (I-1) and comparative examples in table (I-2) to proceed the dyeing and the color fastness to laundering-oxidative bleaching test in example 1. The results were shown in table (II-1) and table (II-2).

table (I-1)

	component (a)	component (b)		component (c)
	Compound ratio	Compound ratio	Compound ratio	Compound ratio
Example 2	(III-1)25%	(V-1)16%	--	(I)59%

Example 3	(III-1) 27%	(V-1) 13%	(VI-1) 6%	(I) 54%
Example 4	(III-1) 27%	(V-3) 18%	--	(I) 55%
Example 5	(III-1) 27%	(V-3) 23%	--	(I) 50%
Example 6	(III-1) 86%	(V-3) 7%	(VIII-2) 7%	--
Example 7	(III-1) 78%	(VI-1) 8%	(X-1) 14%	--
Example 8	(III-1) 74%	(VI-1) 13%	(XI-1) 13%	--
Example 9	(III-1) 74%	(VIII-2) 20%	(IX-2) 6%	--
Example 10	(III-1) 62%	(VIII-2) 25%	(IX-2) 13%	--
Example 11	(III-1) 24%	(VIII-2) 16%	(IX-2) 11%	(I) 49%
Example 12	(III-2) 27%	(V-1) 15%	--	(I) 58%
Example 13	(III-2) 29%	(V-1) 12%	(VI-1) 6%	(I) 53%
Example 14	(III-2) 29%	(V-3) 18%	--	(I) 53%
Example 15	(III-2) 28%	(V-3) 23%	--	(I) 49%
Example 16	(III-2) 88%	(V-3) 6%	(VIII-2) 6%	--
Example 17	(III-2) 79%	(VI-1) 13%	(X-1) 8%	--
Example 18	(III-2) 75%	(VI-1) 12%	(XI-1) 13%	--
Example 19	(III-2) 87%	(VIII-2) 13%	--	--
Example 20	(III-2) 75%	(VIII-2) 19%	(IX-2) 6%	--
Example 21	(III-2) 64%	(VIII-2) 24%	(IX-2) 12%	--
Example 22	(III-2) 25%	(VIII-2) 15%	(IX-2) 11%	(I) 49%
Example 23	(IV-1) 28%	(V-1) 15%	--	(I) 57%

Example 24	(IV-1) 30%	(V-1) 12%	(VI-1) 6%	(I) 52%
Example 25	(IV-1) 30%	(V-3) 17%	--	(I) 53%
Example 26	(IV-1) 29%	(V-3) 22%	--	(I) 49%
Example 27	(IV-1) 88%	(V-3) 6%	(VIII-2) 6%	--
Example 28	(IV-1) 80%	(VI-1) 12%	(X-1) 8%	--
Example 29	(IV-1) 76%	(VI-1) 12%	(XI-1) 12%	--
Example 30	(IV-1) 65%	(VIII-2) 23%	(IX-2) 12%	--
Example 31	(IV-1) 26%	(VIII-2) 15%	(IX-2) 11%	(I) 48%

table (II-1)

	Grade	GIE Lab (ΔE)	CMC (2:1) (ΔE)	On-Tone fading
Example 1	5	0.05	0.21	Y
Example 2	3-4	2.89	2.49	Y
Example 3	3-4	2.84	2.47	Y
Example 4	3-4	2.85	2.32	Y
Example 5	3-4	2.79	2.42	Y
Example 6	4-5	0.63	0.46	Y
Example 7	4-5	0.60	0.44	Y
Example 8	4-5	0.79	0.58	Y
Example 9	4-5	0.45	0.39	Y
Example 10	5	0.35	0.52	Y
Example 11	3-4	2.62	2.32	Y
Example 12	3-4	2.79	2.24	Y
Example 13	3-4	2.61	2.31	Y
Example 14	3-4	2.68	2.28	Y

Example 15	3-4	2.58	2.23	Y
Example 16	4-5	0.51	0.39	Y
Example 17	4-5	0.75	0.60	Y
Example 18	5	0.31	0.31	Y
Example 19	4-5	0.50	0.38	Y
Example 20	4-5	0.40	0.32	Y
Example 21	4-5	0.65	0.53	Y
Example 22	3-4	2.75	2.14	Y
Example 23	3-4	2.65	2.13	Y
Example 24	3-4	2.28	2.09	Y
Example 25	3-4	2.55	2.26	Y
Example 26	3-4	2.39	2.11	Y
Example 27	4-5	1.27	0.96	Y
Example 28	5	0.17	0.29	Y
Example 29	5	0.14	0.30	Y
Example 30	4-5	0.70	0.56	Y
Example 31	3-4	2.27	2.06	Y

table (I-2)

	Component (b)				component (c)
	Compound ratio	Compound ratio	Compound ratio	Compound ratio	Compound ratio
Comparative Example 1	(V-1) 18%	(VI-1) 9%	--	--	(I) 73%
Comparative Example 2	(V-3) 25%	--	--	--	(I) 75%
Comparative Example 3	(V-3) 19%	(V-4) 21%	(VII-1) 3%	--	(I) 57%

Comparative Example 4	(V-4) 22%	(VII-1) 3%	--	--	(I) 75%
Comparative Example 5	(V-4) 18%	(VII-1) 3%	(VIII-2) 17%	(IX-2) 11%	(I) 51%
Comparative Example 6	(VIII-2) 21%	(IX-2) 14%	--	--	(I) 65%

table (II-2)

	Grade	GIE Lab (ΔE)	CMC (2:1) (ΔE)	On-Tone fading
Comparative Example 1	3	3.61	2.78	N
Comparative Example 2	3	4.88	3.31	N
Comparative Example 3	3	3.16	2.95	N
Comparative Example 4	2-3	4.33	3.21	N
Comparative Example 5	3	3.19	2.80	N
Comparative Example 6	3	4.94	3.15	N

The black dye composition of the present invention can be widely applied to dyeing a greater range of textiles that contain a hydroxyl group or an amide group. The composition of the present invention can be used in traditional dyeing methods, for example, exhaustion, printing, or continuous dyeing.

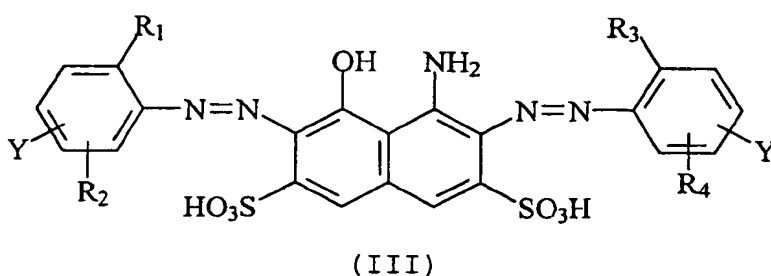
For cellulose fiber, the black dye composition of the present invention is a dye composition with great industrial value. It has good properties in build-up, wash fastness, ease of wash-off, and levelness, especially excellently performing
5 in the properties of good color fastness to laundering-oxidative bleach.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and, without departing from the scope thereof, can
10 make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

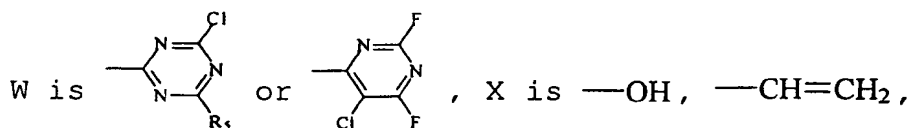
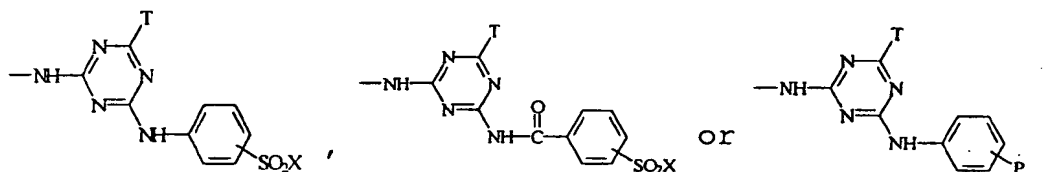
What is Claimed is

1. A reactive dye composition having good color fastness to laundering-oxidative bleach which comprises:

- (a) at least a black or navy reactive dye with a good color fastness to laundering-oxidative bleach, said black or navy reactive dye is selected from the group consisting of formula (III)

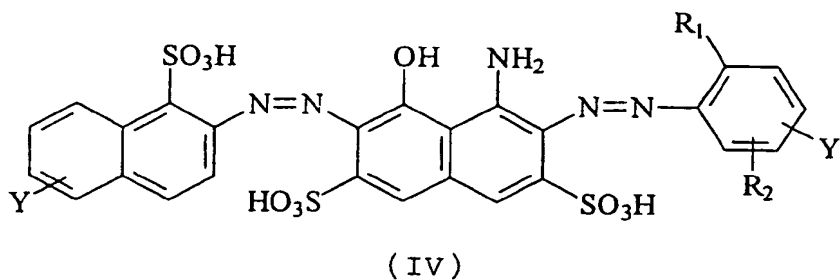


wherein Y and Y', each independent, is $-\text{SO}_2\text{X}$, $-\text{NH}-\text{W}$,



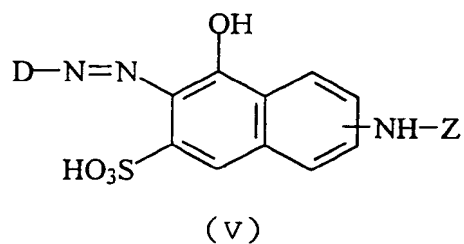
$-\text{C}_2\text{H}_4\text{OSO}_3\text{H}$, or $-\text{C}_2\text{H}_4\text{Cl}$, T is $-\text{NHCN}$, $-\text{F}$ or $-\text{Cl}$, P is hydrogen, halogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, R_5 is C_1 - C_4 alkoxy, R_1 , R_2 , R_3 and R_4 , each independent, is hydrogen, halogen, hydroxyl, C_1 - C_4 alkyl C_1 - C_4 alkoxy, or sulfonyl groups and at

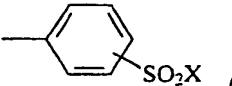
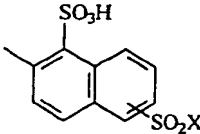
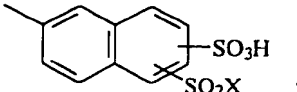
least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen,
or formula (IV)

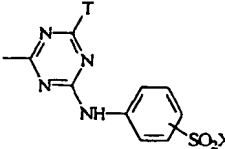
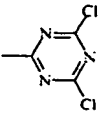
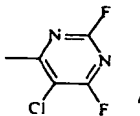


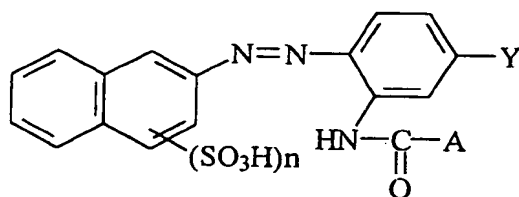
wherein Y, Y', R_1 and R_2 are defined as the above; and

(b) at least a red, orange, yellow or other shade of
reactive azo dye, said red, orange, yellow or other shade of
reactive azo dye is selected from the group consisting of formula
(V), formula (VI), formula (VII), formula (VIII), formula
(IX), formula (X) or formula (XI),



wherein D is ,  or ,

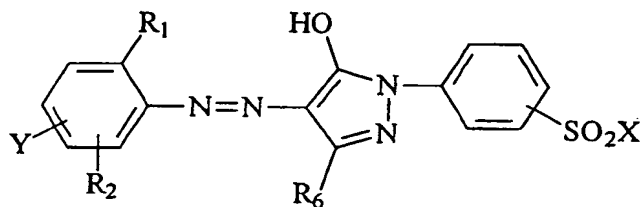
Z is $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$, , , or ,
 X and T are defined as the above,



5

(VI)

wherein Y is defined as the above, n is 1, 2, or 3, A is $-\text{OH}$,
 $-\text{NH}_2$, or $-\text{CH}_3$,

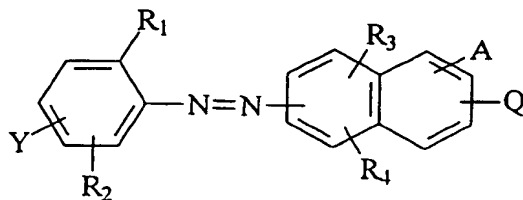


10

(VII)

wherein X, Y, R₁, and R₂ are defined as the above, R₆ is $-\text{CO}_2\text{H}$,
 $-\text{NH}_2$, or $-\text{CH}_3$,

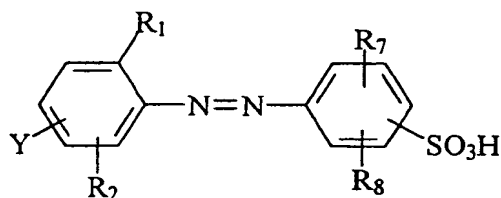
15



(VIII)

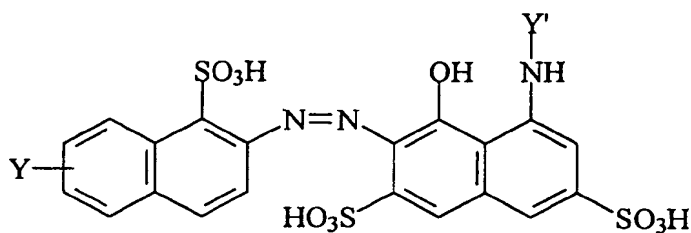
wherein Y, R₁, R₂, R₃, R₄ and A are defined as the above, Q is
—CO₂H, or —SO₃H,

5



(IX)

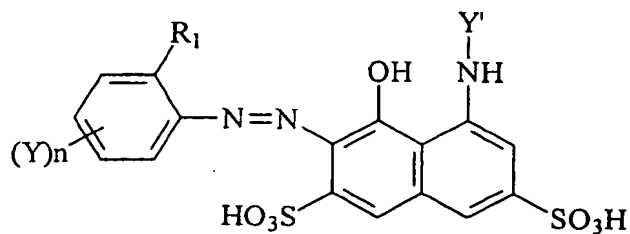
wherein Y, R₁, and R₂ are defined as the above, R₇ and R₈ each
10 independent is hydrogen, C₁-C₄ alkyl, amino or amino
derivatives,



(X)

15

wherein Y and Y' are defined as the above,



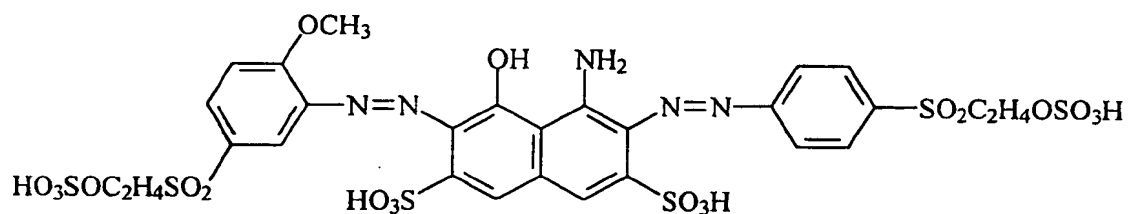
(XI)

wherein n , Y , Y' and R_1 are defined as the above.

5 2. The composition of claim 1, wherein said black or navy reactive dye of component (a) is selected from the formula (III).

3. The composition of claim 1, wherein said black or deep navy reactive dye of component (a) is selected from the formula (IV).

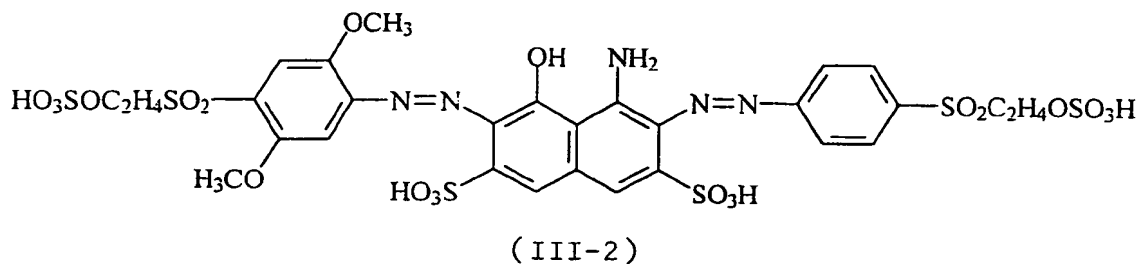
10 4. The composition of claim 2, wherein said formula (III) is the following formula (III-1).



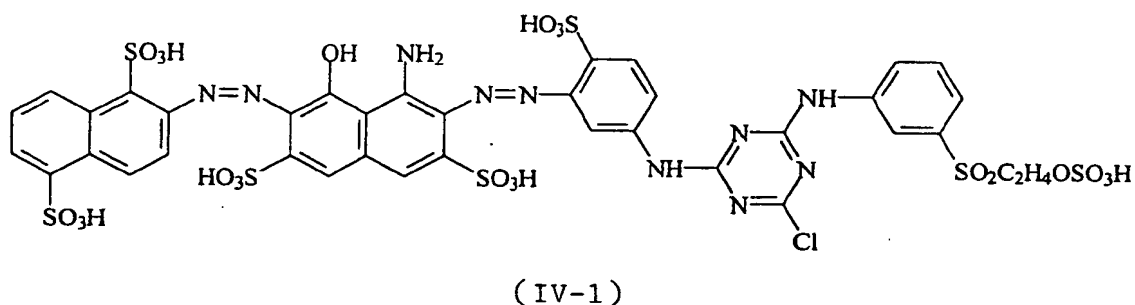
(III-1)

15

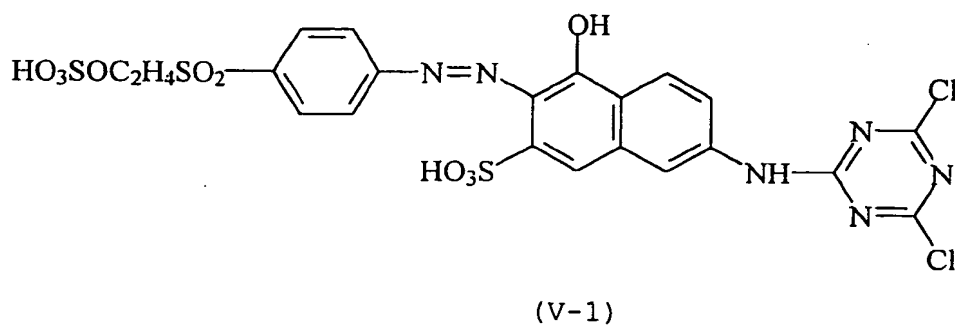
5. The composition of claim 2, wherein said formula (III) is the following formula (III-2).



6. The composition of claim 3, wherein said formula (IV)
5 is the following formula (IV-1).

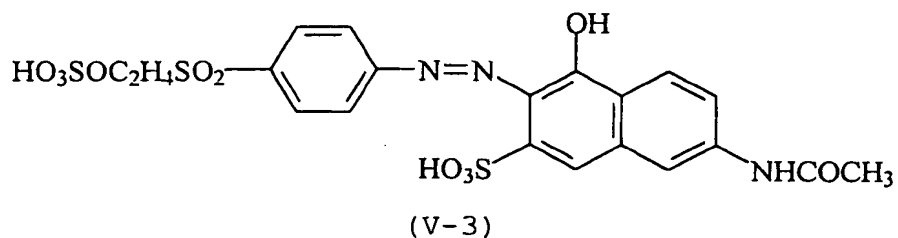


10 7. The composition of claim 1, wherein said formula
(V) is the following formula (V-1).

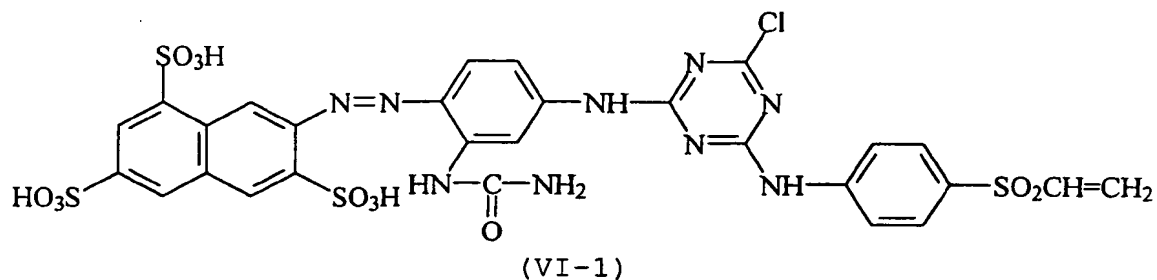


15

8. The composition of claim 1, wherein said formula
(V) is the following formula (V-3).

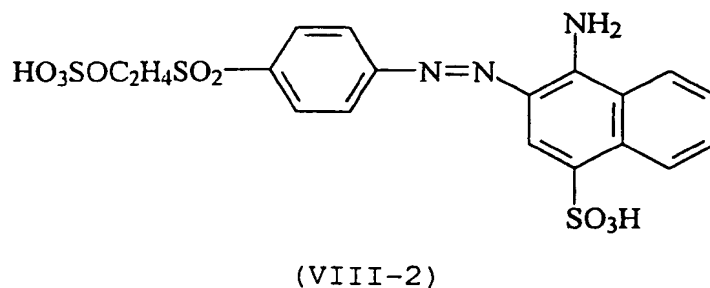


- 5 9. The composition of claim 2, wherein said formula (VI) is the following formula (VI-1).



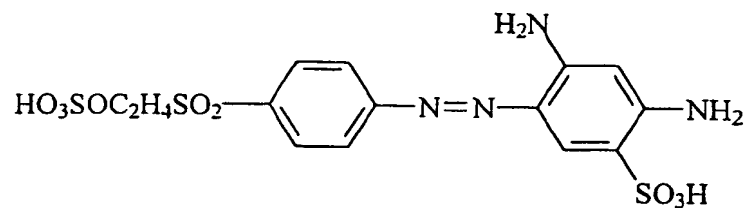
10

10. The composition of claim 1, wherein said formula (VIII) is the following formula (VIII-2).



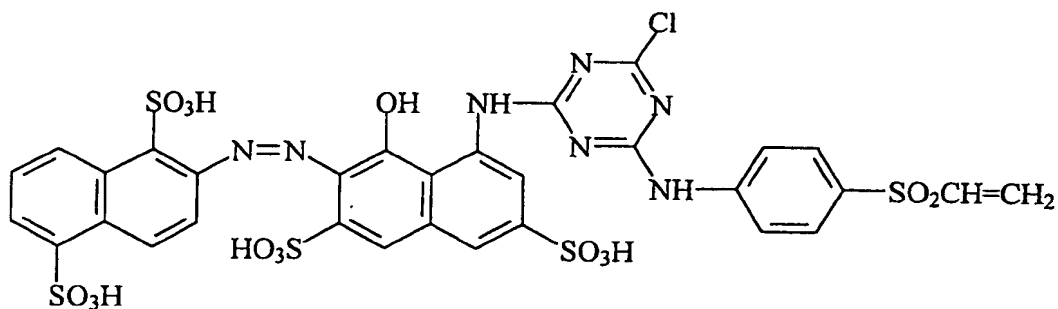
15

11. The composition of claim 1, wherein said formula (IX) is the following formula (IX-2).



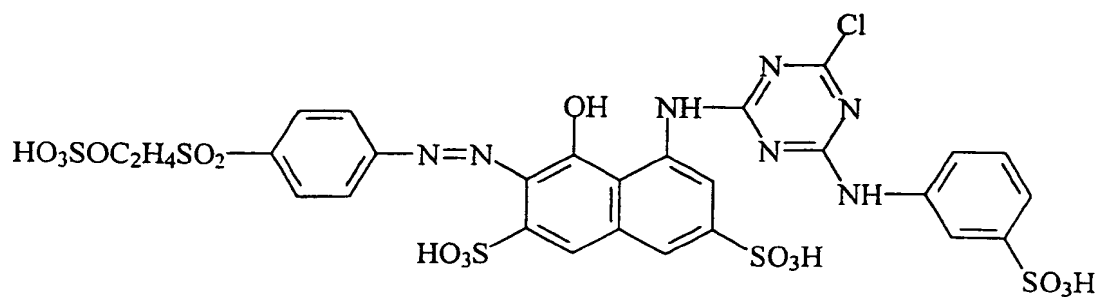
(IX-2)

12. The composition of claim 1, wherein said formula (X)
 5 is the following formula (X-1).



(X-1)

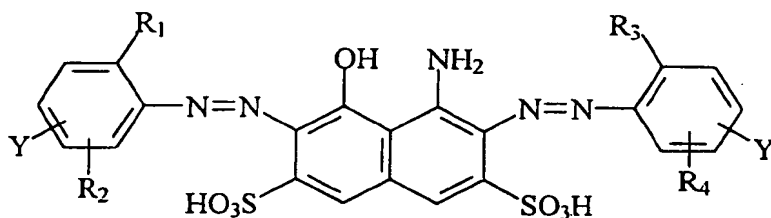
10 13. The composition of claim 1, wherein said formula
 (XI) is the following formula (XI-1).



(XI-1)

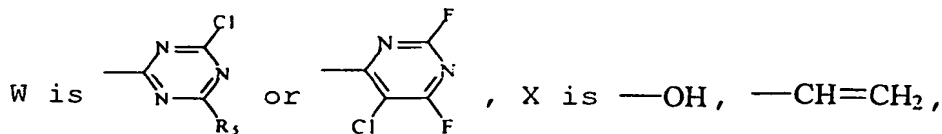
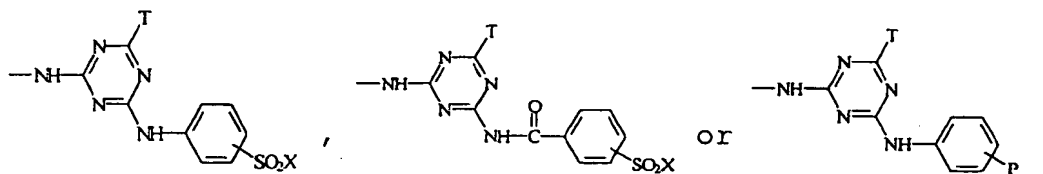
14. A reactive dye composition which comprises:

- (a) at least a black or navy reactive dye with a good
 5 color fastness to laundering-oxidative bleach, said black or
 navy reactive dye is selected from the group consisting of
 formula (III)



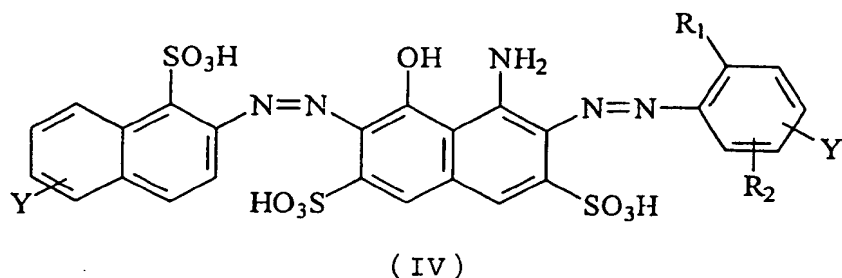
(III)

wherein Y and Y', each independent, is $\text{—SO}_2\text{X}$, —NH—W ,



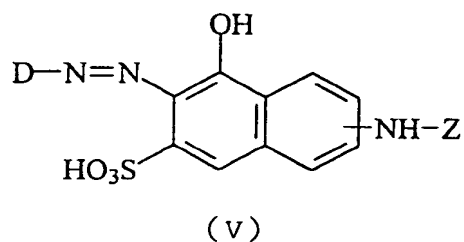
$\text{—C}_2\text{H}_4\text{OSO}_3\text{H}$ or $\text{—C}_2\text{H}_4\text{Cl}$, T is —NHCN , —F or —Cl , P is hydrogen,
 halogen, $\text{C}_1\text{—C}_4$ alkyl or $\text{C}_1\text{—C}_4$ alkoxyl, R_5 is $\text{C}_1\text{—C}_4$ alkoxyl,
 20 R_1 , R_2 , R_3 and R_4 , each independent, is hydrogen, halogen,

hydroxyl, C₁-C₄ alkyl C₁-C₄ alkoxy, or sulfonyl groups and at least one of R₁, R₂, R₃ and R₄ is other than hydrogen, or formula (IV)

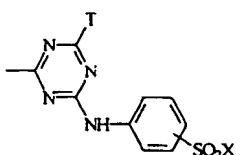
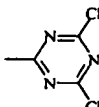
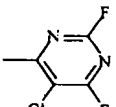


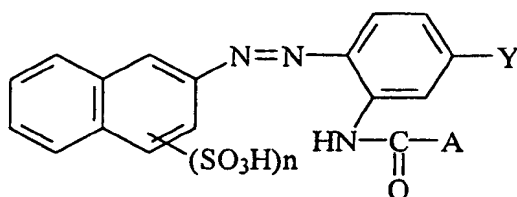
wherein Y, Y', R₁ and R₂ are defined as the above; and

(b) at least a red, orange, yellow or other shade of
 10 reactive azo dye, said red, orange, yellow or other shade of reactive azo dye is selected from the group consisting of formula (V), formula (VI), formula (VII), formula (VIII), formula (IX), formula (X) or formula (XI),



wherein D is , or ,

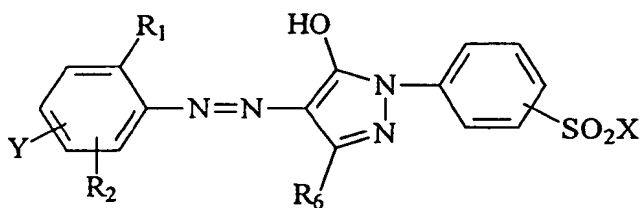
Z is $\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$, $\text{—}\overset{\text{O}}{\parallel}\text{C—C}_2\text{H}_5$,  ,  or  ,
 X and T are defined as the above,



5

(VI)

wherein Y is defined as the above, n is 1, 2, or 3, A is —OH ,
 —NH_2 , or —CH_3 ,

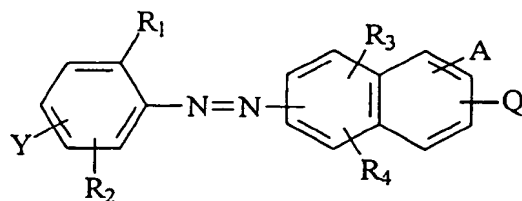


10

(VII)

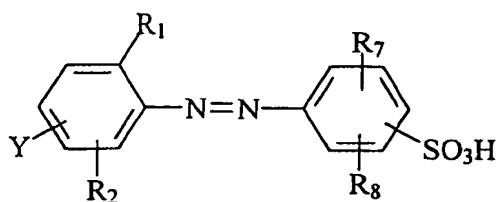
wherein X, Y, R₁, and R₂ are defined as the above, R₆ is $\text{—CO}_2\text{H}$,
 —NH_2 , or —CH_3 ,

15



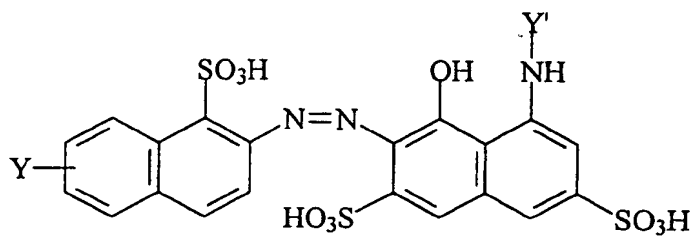
(VIII)

wherein Y, R₁, R₂, R₃, R₄ and A are defined as the above, Q is
 5 —CO₂H, or —SO₃H,



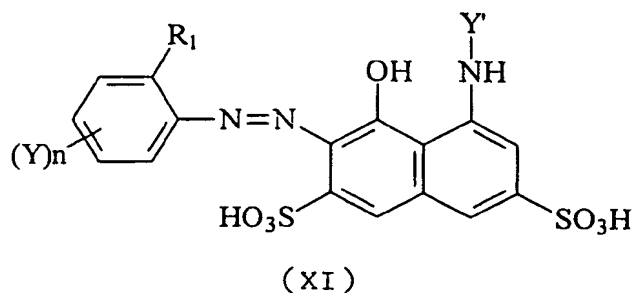
(IX)

10 wherein Y, R₁, and R₂ are defined as the above, R₇ and R₈, each independent, is hydrogen, C₁-C₄ alkyl, amino or amino derivatives,



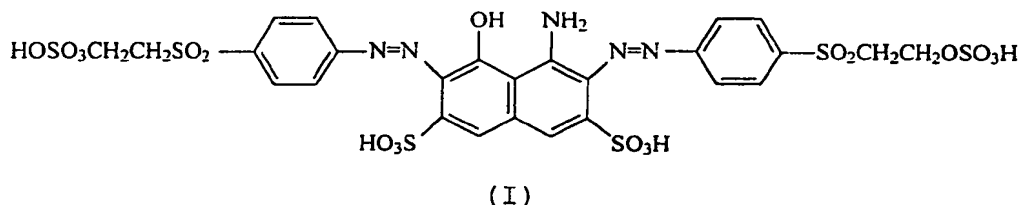
(X)

wherein Y and Y' are defined as the above,



wherein n , Y , Y' and R_1 are defined as the above; and

5 (c) a black reactive dye of the following formula (I).

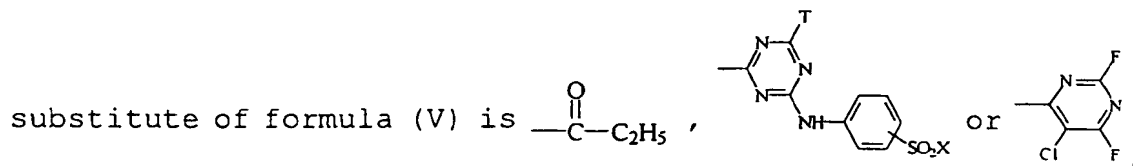


10 15. The composition of claim 14, which is a composition having good color fastness to laundering-oxidative bleach.

16. The composition of claim 14 or 15, wherein said black or navy reactive dye of component (a) is selected from the formula (III).

15 17. The composition of claim 14 or 15, wherein said black or deep navy reactive dye of component (a) is selected from the formula (IV).

18. The composition of claim 14 or 15, wherein said Z

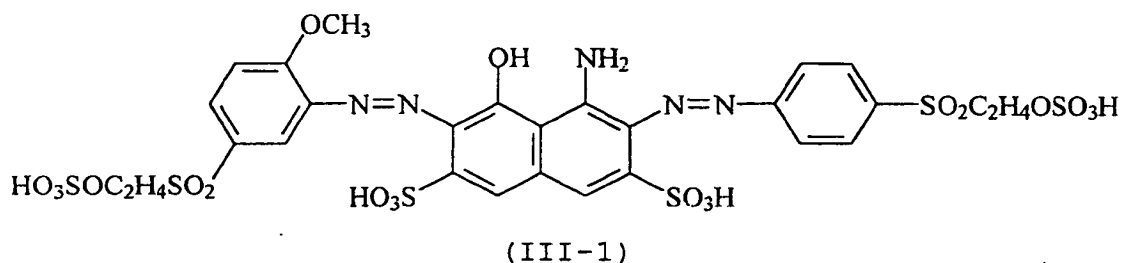


20

wherein X and T are defined as the above.

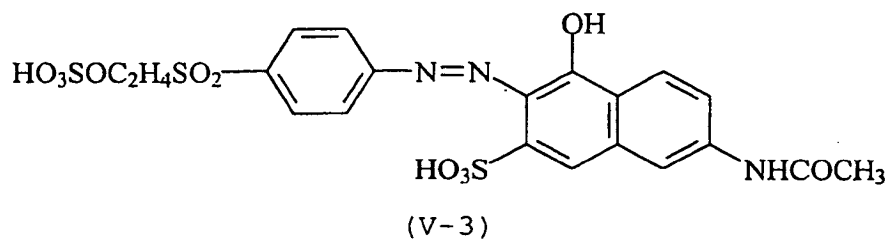
19. The composition of claim 14 or 15, wherein said R_1 , R_2 , R_3 and R_4 of the formula (III), each independent, is hydrogen, halogen, hydroxyl, C_1 - C_4 alkyl, or sulfonyl groups and at least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen.

5 20. The composition of claim 4 comprising formula (III-1)



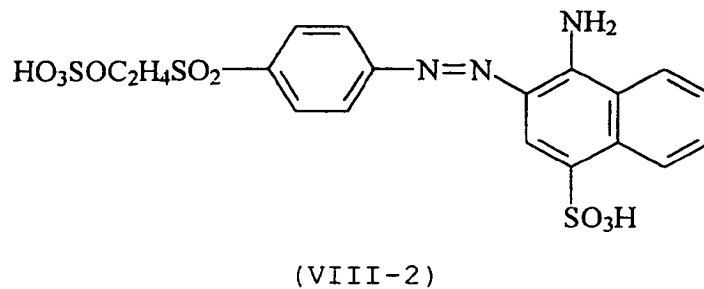
10

10% to 95% by weight, formula (V-3)



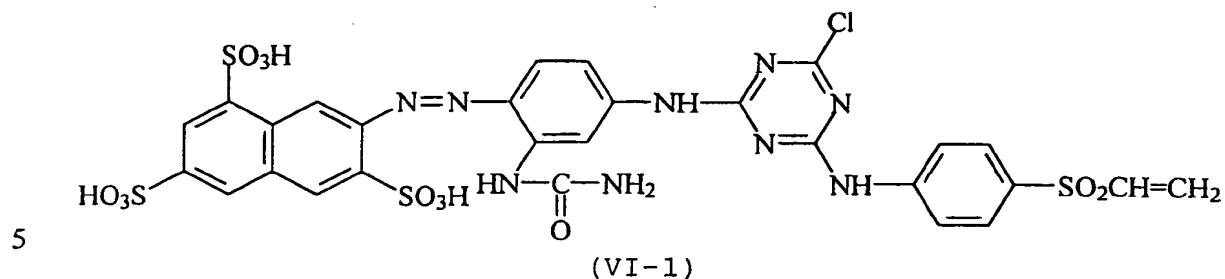
15

3% to 40% by weight, and formula (VIII-2)

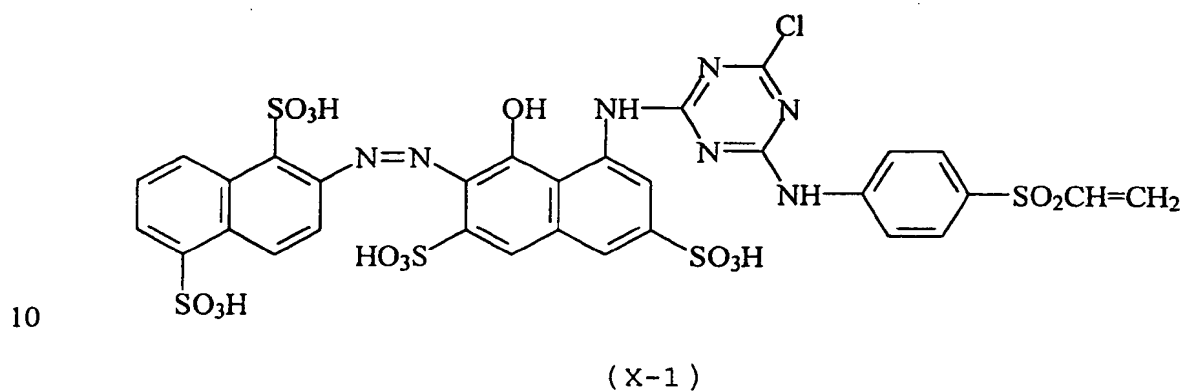


3% to 40% by weight.

21. The composition of claim 4 comprising formula (III-1)
10% to 95% by weight, formula (VI-1)

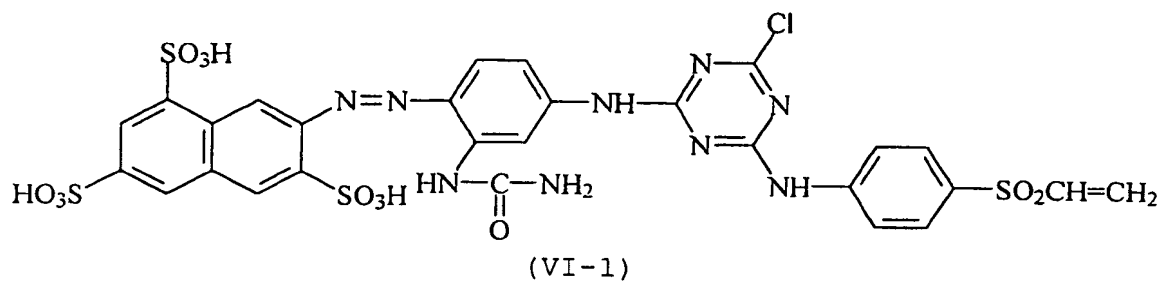


3% to 40% by weight, and formula (X-1)



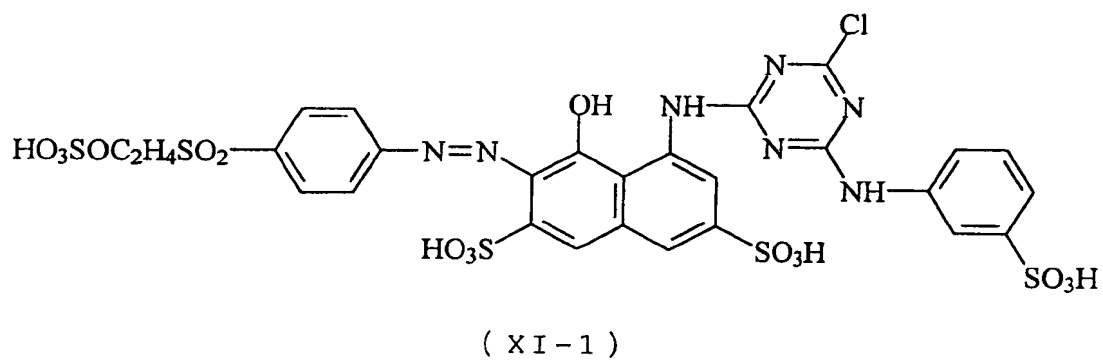
3% to 40% by weight.

22. The composition of claim 4 comprising formula (III-1)
15 10% to 95% by weight, formula (VI-1)



3% to 40% by weight, and formula (XI-1)

5

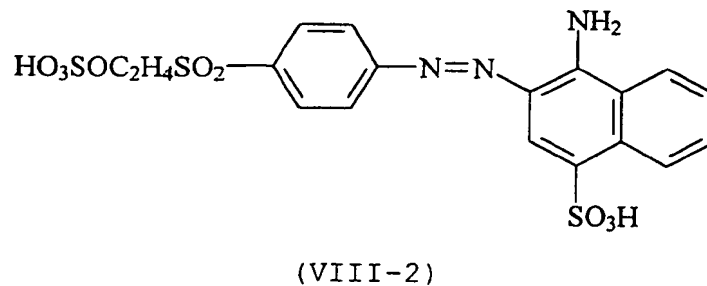


3% to 40% by weight.

10

23. The composition of claim 4 comprising formula (III-1)

10% to 95% by weight and formula (VIII-2)

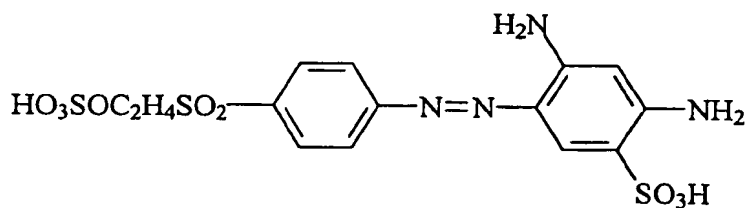


15

3% to 40% by weight.

24. The composition of claim 4 comprising formula (III-1)
10% to 95% by weight, formula (VIII-2) 3% to 40% by weight, and
formula (IX-2)

5



(IX-2)

3% to 40% by weight.

10 25. The composition of claim 5 comprising formula (III-2)
10% to 95% by weight, formula (V-3) 3% to 40% by weight, and
formula (VIII-2) 3% to 40% by weight.

26. The composition of claim 5 comprising formula (III-2)
10% to 95% by weight, formula (VI-1) 3% to 40% by weight, and
15 formula (X-1) 3% to 40% by weight.

27. The composition of claim 5 comprising formula (III-2)
10% to 95% by weight, formula (VI-1) 3% to 40% by weight, and
formula (XI-1) 3% to 40% by weight.

28. The composition of claim 5 comprising formula (III-2)
20 10% to 95% by weight and formula (VIII-2) 3% to 40% by weight.

29. The composition of claim 5 comprising formula (III-2) 10% to 95% by weight, formula (VIII-2) 3% to 40% by weight, and formula (IX-2) 3% to 40% by weight.

30. The composition of claim 6 comprising formula (IV-1) 10% to 95% by weight, formula (V-3) 3% to 40% by weight, and formula (VIII-2) 3% to 40% by weight.

31. The composition of claim 6 comprising formula (IV-1) 10% to 95% by weight, formula (VI-1) 3% to 40% by weight, and formula (X-1) 3% to 40% by weight.

32. The composition of claim 6 comprising formula (IV-1) 10% to 95% by weight, formula (VI-1) 3% to 40% by weight, and formula (XI-1) 3% to 40% by weight.

33. The composition of claim 6 comprising formula (IV-1) 10% to 95% by weight, formula (VIII-2) 3% to 40% by weight, and formula (IX-2) 3% to 40% by weight.

34. The composition of claim 14 comprising formula (I) 10% to 95% by weight, formula (III-1) 10% to 95% by weight, formula (VIII-2) 3% to 40% by weight, and formula (IX-2) 3% to 40% by weight.

35. The composition of claim 15 comprising formula (I) 10% to 95% by weight, formula (III-1) 10% to 95% by weight, formula (VIII-2) 3% to 40% by weight, and formula (IX-2) 3% to

40% by weight.

36. The composition of claim 15 comprising formula (I) 10% to 95% by weight, formula (III-1) 10% to 95% by weight, and formula (V-1) 3% to 40% by weight.

5 37. The composition of claim 15 comprising formula (I) 10% to 95% by weight, formula (III-1) 10% to 95% by weight, formula (V-1) 3% to 40% by weight and formula (VI-1) 3% to 40% by weight.

38. The composition of claim 15 comprising formula (I) 10 10% to 95% by weight, formula (III-1) 10% to 95% by weight, and formula (V-3) 3% to 40% by weight.

39. The composition of claim 14 comprising formula (I) 10% to 95% by weight, formula (III-2) 10% to 95% by weight, formula (VIII-2) 3% to 40% by weight, and formula (IX-2) 3% to 15 40% by weight.

40. The composition of claim 14 comprising formula (I) 10% to 95% by weight, formula (IV-1) 10% to 95% by weight, and formula (V-1) 3% to 40% by weight.

41. The composition of claim 14 comprising formula (I) 20 10% to 95% by weight, formula (IV-1) 10% to 95% by weight, formula (V-1) 3% to 40% by weight, and formula (VI-1) 3% to 40% by weight.

42. The composition of claim 14 comprising formula (I)

10% to 95% by weight, formula (IV-1) 10% to 95% by weight, and formula (V-3) 3% to 40% by weight.

43. The composition of claim 14 comprising formula (I) 10% to 95% by weight, formula (IV-1) 10% to 95% by weight, formula
5 (VIII-2) 3% to 40% by weight, and formula (IX-2) 3% to 40% by weight.

44. The composition of claim 15 comprising formula (I) 10% to 95% by weight, formula (III-2) 10% to 95% by weight, and formula (V-1) 3% to 40% by weight.

10 45. The composition of claim 15 comprising formula (I) 10% to 95% by weight, formula (III-2) 10% to 95% by weight, formula (V-1) 3% to 40% by weight, and formula (VI-1) 3% to 40% by weight.

46. The composition of claim 15 comprising formula (I)
15 10% to 95% by weight, formula (III-2) 10% to 95% by weight, and formula (V-3) 3% to 40% by weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/00486

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : IPC7 - C09B 67/22, 67/24

US CL : 8/549, 641

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/549, 641

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA online

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 7-278461A (MITSHBISHI KASEI HOECHST KK) 24 October 1995, see col 7 and 8.	1,2,4,5,8, 10,11, 14-16, 19- 20
Y	US 5,611,821A (HUANG et al.) 18 March 1997, see abstract and col 5 and 6.	1 , 2 , 4 , 5 , 1 0 11,14,15, 16,19,20
Y	JP 9-169922A (SUMITOMO CHEMICAL CO. LTD) 30 June 1997, see all of col 15 and 16.	1,2,4,5,8,1 4,16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

05 APRIL 2000

Date of mailing of the international search report

26 APR 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

MARGARET EINSMANN

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/00486

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 24-46
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

the claims contain reference to chemical formulae by reference to Roman numerals only. Said structures are not defined in the claims on which they are dependent and thus the claims are incomplete negating a search.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/00486

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, Claims 1-5,8,10,11,14-17,19,20,23 when limited to dye mixtures consisting of dyes wherein Y and Y' are vinyl sulfonyl reactive groups (SO₂X where X is -OH, -CH=CH₂, -C₂H₄OSO₃H or -C₂H₄Cl)

Group II, Claims 1-3,7,13-17,19 when limited to dye mixtures consisting of dyes wherein Y and Y' are halotriazine reactive groups not substituted by another reactive group.

Group III, Claims 1-3, 14-19 when limited to dye mixtures consisting of dyes wherein Y and Y' are difluoro, chloropyrimidine reactive groups.

Group IV, Claims 1-3,,6,7,9,12,13-18,21-22 when limited to dyes wherein Y and Y' are halotriazine reactive groups reactively bonded via a bridge member to vinylsulfonyl reactive groups.

The inventions listed as Groups I-IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The reactive groups are structurally dissimilar, relating to two distinct nitrogen heterocycle-type compounds, a sulfur containing straight chain compounds, as well as a group having both nitrogen heterocycle and straight chain sulfur containing moieties. and although they comprise fiber reactive dyes, they have different activities and modes of operation. Although they have been grouped together in generic claim 1, the structures of the reactive groups are so dissimilar that they cannot be considered to be in a genus-species relationship, nor can they be considered as being one invention.

THIS PAGE BLANK (USPTO)